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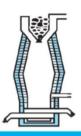
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Pyrometallurargical Extraction

Concept of the month

This column is aimed at preparing students for all competitive exams like JEE, NEET, BITSAT etc. Every concept has been designed by highly qualified faculty to cater to the needs of the students by discussing the most complicated and confusing concepts in Chemistry.

> By: P. BRAHMA REDDY (Alumni from IIT Delhi)

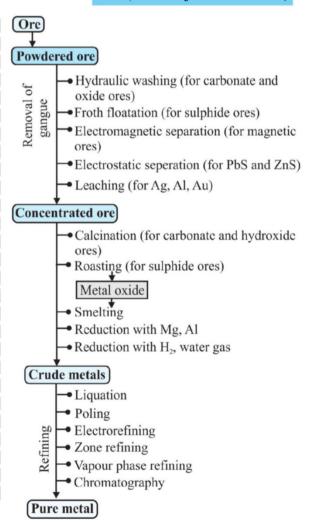
Introduction

- O The process of extraction of metal from its ores in I profitable manner is called metallurgy.
- Mineral is a substance in which metal is present in either native state or in combined state.
- **Ore** is the mineral from which the metal can be economically and conveniently extracted.
- O Gangue or matrix is the impurities present in the
- Extraction of pure metal from its ore done in various steps, which are given in the flow chart.

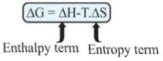
In this article much focus given towards the extraction of some metals based on thermodynamic principles i.e., pyrometallurigcal process.

Thermodynamic principles in extraction of metals

- O In metallurgical operations the selection of a | suitable, reducing agent for reduction of a particular | oxide can be decided on the basis of thermodynamic principles.
- The optimum temperature at which reduction can occur smoothly can also be predicted using thermodynamic principle.
- O The Gibbs free energy change ΔG of a reaction is a measure of the thermodynamic driving force that makes a reaction occur. A negative value for ΔG indicates that a reaction can proceed spontaneously without any external inputs, while a positive value indicates that it will not.



O For feasibility of any reaction at any temperature \mid the value of ΔG must be negative at that temperature.



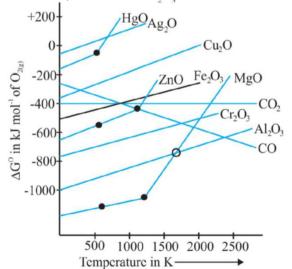
 ΔH : – Measure of actual energy that is liberated when the reaction occurs.

 ΔS : – Measure of the change in the possibilities for disorder in the products compared to the reactants.

- O Greater the negative value of ΔG , higher is the reducing power of an element.
- O For the reduction of a metal oxide with a reducing agent, the plot of ΔG^o vs temperature is studied, which is called Ellingham diagram.

Characteristics of Ellingham diagram

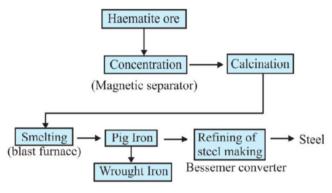
- O ΔG^o becomes more positive when temperature increases, i.e., stability of oxides decreases.
- O A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, i.e., the metals for which the free energy of formation (ΔG^{o}) of their oxides is more negative can reduce those metal oxides which has less negative ΔG^{o} . Thus, Al reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773K.
- O CO is more effective reducing agent below 1073K and above 1073K coke is more effective reducing agent, e.g., CO reduces Fe₂O₃ below 1073K but above it, coke reduces Fe₂O₃.



Extraction of Iron

O **Ores**: Haematite – Fe₂O₃ Limonite – 2Fe₂O₃. 3H₂O; Siderite FeCO₃; Magnetite – Fe₃O₄, Pyrite-FeS₂.

O Process:



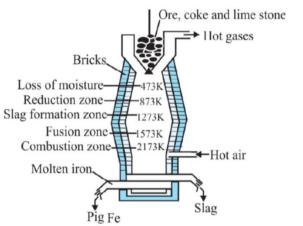


Fig:Blast furnace

O Reactions:

(i) Roasting: FeO changes to Fe₂O₃ to prevent the loss of iron during smelting.

$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

(ii) Smelting (In blast furnace):

In reduction zone:

At 400°C, 3Fe₂O₃ + CO
$$\rightarrow$$
 2Fe₃O₄ + CO₂

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

At 600° C, $FeO + CO \rightarrow Fe + CO$

$$CaCO_3 \rightarrow CaO + CO_5$$

In central zone:

$$FeO+3CO \rightarrow 2CO_2 + C + Fe$$

(900 – 1200°C) Fe acts as catalyst here and 'C' so formed is dissolved in Fe.

$$\underset{(flux)}{CaO} + \underset{(impurity)}{SiO_2} \rightarrow \underset{(slag)}{CaSiO_3}$$

In fusion zone

$$CO_2 + C \rightarrow 2CO, \Delta H = +ve$$

(1100 – 1200°C) melting of iron takes place In combustion zone

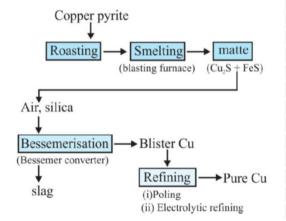
$$2C + O_2 \rightarrow 2CO$$
, $\Delta H = -ve$

 $(1500 - 1600^{\circ}C)$

- \bigcirc Pig Iron: C-3.1-4.5%, small amounts of Si, S, P; hard and brittle, obtained from blast furnace
- **Wrought Iron:** C 0.15 0.28%, purest form; malleable, fibrous
- \bigcirc Steel: C 0.15 1.5%, strength is high.

Extraction of Copper

- Ores: Copper pyrites CuFeS, ; Cuprite or ruby copper Cu₂O; Copper glance Cu₂S; Malachite Cu (OH), . CuCO, ; Azurite Cu (OH), . 2CuCO,.
- O Process:



O Reactions:

(i) Roasting:

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

(ii) Smelting:

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

 $FeO + SiO_2 \rightarrow FeSiO_3$

(iii) Bessemerisation:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

 $FeO + SiO_2 \rightarrow FeSiO_3$

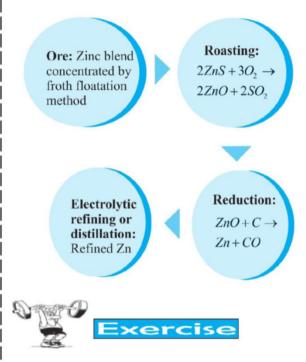
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$
 (self reduction)

- O Poling: Molten Cu is stirred with poles of green wood to reduce any copper oxide in Copper
- O Electrolytic refining: Anode impure Cu; cathode - pure Cu; electrolyte - CuSO₄ + H₂SO₄.

Note: Copper can be extracted by hydrometallurgical process also

Extraction of Zinc



- 1. Composition of azurite mineral is
 - (a) CuCO₃.CuO
- (b) $Cu(HCO_3)_{\gamma}.Cu(OH)_{\gamma}$
- (c) $2CuCO_3.Cu(OH)$, (d) $CuCO_3.2Cu(OH)$,
- 2. The process is used to remove reductible oxides from metals. Molten impure metal is stirred by a wooden rods. The hydrocarbon gases reduce the oxides. The process is called
 - (a) Zone refining
- (b) Cupellation
- (c) Poling
- (d) Leaching
- 3. Roasted copper pyrite on smelting with sand produces
 - (a) FeSiO₂ as fusible slag and Cu₂S as matte
 - (b) CaSiO₃ as infusible slag and Cu₂O as matte
 - (c) Ca₃(PO₄), as fusible slag and Cu₂S as matte
 - (d) Fe₃(PO₄)₂ as infusible slag and Cu₂S as matte

4. Which series of reactions correctly represents chemical relations related to iron and its compound?

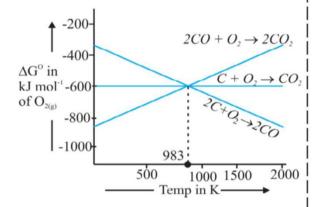
(a)
$$Fe \xrightarrow{O_2,heat} Fe_3O_4 \xrightarrow{CO,600^{\circ}C} FeO \xrightarrow{CO,700^{\circ}C} Fe$$

$$\text{(b) } \textit{Fe} \xrightarrow{\textit{dil } \textit{H}_2 \textit{SO}_4} \rightarrow \textit{FeSO}_4 \xrightarrow{\textit{H}_2 \textit{SO}_4, \textit{O}_2} \rightarrow \textit{Fe}_2 \big(\textit{SO}_4\big)_3 \xrightarrow{\textit{heat}} \textit{Fe}$$

(c)
$$Fe \xrightarrow{O_2,heat} FeO \xrightarrow{dil.H_2SO_4} FeSO_4 \xrightarrow{heat} Fe$$

(d)
$$Fe \xrightarrow{Cl_2,heat} FeCl_3 \xrightarrow{heat,air} FeCl_2 \xrightarrow{Zn} Fe$$

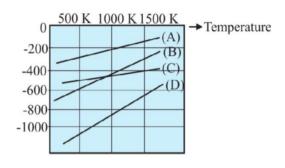
5.



From the given Ellingham diagram which is a better reducing agent at 673k?

(a) C

- (b) CO
- (c) CO₂
- (d) Any of these
- **6.** Why are the slopes of many of the lines on the Ellingham diagram almost identical?
 - (a) Most reactions involve the elimination of one mole of gas, so there is a similar standard enthalpy change of a reaction.
 - (b) Most reactions involve the elimination of one mole of gas, so there is a similar standard entropy change of a reaction.
 - (c) The activity of the most of the metals is same.
 - (d) The partial pressure of the reacting gas is the same for all reactions.
- 7. For Fe₂O₄ (solid), standard enthalpy of formation is -1120 kJ mol⁻¹. Change in entropy, under standard conditions, for the formation of 1 mol of Fe₂O₄ is -350 J K⁻¹ mol⁻¹. Which of the following graphs is the Ellingham diagram for Fe₃O₄?



- (a) A (b) B (c) C (d) D 8. In the extraction of iron metal from haematite ore,
- CaCO₂ (lime stone) is one of the constituents of the charge. The role of CaCO₃ in the extraction
 - (a) reduce oxides of iron by providing CO₂ gas
 - (b) oxidize the metallic impurities to respective
 - (c) lower the temperature at which haematite gets reduced to iron
 - (d) provide CaO to gangue which is separated as
- **9.** Which is NOT true for both (A) extraction of iron from haematite ore and (B) extraction of tin from tin stone (cassiterite)?
 - (a) The ore is an oxide ore
 - (b) Pyrometallurgical extractive method is used for extraction of the metal from the ore
 - (c) The function of C is to act as a reducing agent
 - (d) Purification is carried out by zone melting
- 10. Highly electropositive metals cannot be extracted by carbon reduction process because these:
 - (a) Metals do not react with carbon
 - (b) Metals do not combine with carbon to form carbides
 - (c) Metal oxides are not reduced by carbon
 - (d) Loss of metal is more by vaporisation
- 11. Statement-I: Carbon monoxide is capable of reducing FeO to Fe at certain temperature. Statement-II: At the given temperature, standard

free energy of reaction, $2Fe + O_2 \rightarrow 2FeO$ is more negative compared to the standard free energy of the reaction, $2CO + O_2 \rightarrow 2CO_2$

- (a) Statement-I and Statement-II are true and Statement-II is the correct explanation of Statement-I.
- (b) Statement-I and Statement-II are true, but Statement-II is not the correct explanation of

Statement -I

- (c) Statement-I is true, but Statement -II is false
- (d) Statement-I is false, but Statement -II is true
- 12. Statement-I: The precious metal, silver present as impurity in the metal lead may be recovered by treating molten impure lead with molten zinc. Statement-II: Under equilibrium conditions, in a mixture of two immiscible liquids (molten lead and molten zinc), when silver is dissolved, the concentration of silver in molten zinc is much higher than its concentration in molten lead.
 - (a) Statement-I and Statement-II are true and Statement-II is the correct explanation of Statement-I.
 - (b) Statement-I and Statement-II are true, but Statement-II is not the correct explanation of
 - (c) Statement-I is true, but Statement -II is false
 - (d) Statement-I is false, but Statement -II is true
- 13. Consider the following reactions at 1000°C

(1)
$$Zn(s) + \frac{1}{2}O_2(g) \to ZnO(s)$$
 $\Delta G^\circ = -360 \text{ kJ mol}^{-1}$

(2)
$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta G^\circ = -460 \text{ kJ mol}^{-1}$$

Choose the correct statement at 1000°C

- (a) Zinc can be oxidized by CO.
- (b) Zinc oxide can be reduced by carbon
- (c) Both statements A and B are true
- (d) Both statements A and B are false
- Consider the oxidation reaction

$$\frac{2x}{y} \underbrace{M}_{Metal(s)} + \underbrace{O_2}_{(g)} \rightarrow \frac{2}{y} \underbrace{M}_{x} \underbrace{O_y}_{Metal \ oxide(s)}$$

Choose the incorrect statement.

- (a) Oxygen has higher entropy than the metal but lesser entropy than the metal oxide.
- (b) ΔS^{o} for the oxidation reaction would be negative
- (c) ΔG° would become less and less negative with increase in temperature
- (d) If the temperature is very high, ΔG° may become zero, and even positive.

- 15. Column-I Column-II (Reaction) (Temperature)
 - (i) $CaO + SiO_2 \rightarrow CaSiO_3$ (P) 1000°C
 - (ii) $C + CO_2 \rightarrow 2CO$ (Q)900°C
 - (iii) $CaCO_2 \rightarrow CaO + CO_2$ (R) 400°C
 - (iv) $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ (S) 1800°C

ANSWER KEY

1. c **2.** c **3.** a **4.** a 5. b 6. b 7. c 8. d **9.** d **10.** d 11. c **12.** a 13. b 14. a 15. (i) \rightarrow (Q), (ii) \rightarrow (P), (iii) \rightarrow (Q), (iv) \rightarrow (R)

HINTS & SOLUTIONS

- **1.Sol:** Azurite is a basic copper carbonate ore having composition $2CuCO_2.Cu(OH)_2$.
- 3.Sol: During smelting, silica combines with FeO to form fusible FeSiO₃ slag and Cu₂S as matte.
- **4.Sol:**Combustion of Fe to give Fe₃O₄ which upon reduction with CO first gives FeO and finally Fe. Option (b) and (c) are wrong because FeSO₄ and Fe₂(SO₄)₃ on heating gives Fe₂O₃.SO₂.SO₃ and not

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_3 + SO_2$$

Option (d) is wrong because in presence of air, reduction of FeCl, to FeCl, cannot occur.

5.Sol: From the diagram ΔG° for formation of CO, from CO is more -ve than formation of CO (or) CO, from carbon at 673K.

Hence CO is a better reductant than C at 673K.

- **6.Sol:** Most of the reactions have similar ΔS^o value.
- 11.Sol: At the given temperature, free energy of reaction, $2Fe + O_2 \rightarrow 2FeO_2$, is LESS negative.

MOLECULAR ORBITAL THEORY

- 1. While filling electrons in $\pi 2 p_x$ and $\pi 2 p_y$ the electronic configuration rules that has to be followed
 - (a) Pauli's exclusion principle
 - (b) Aufbau principle
 - (c) Both Pauli's and Hund's rule
 - (d) All the above
- 2. The paramagnetic nature of oxygen is best explained
 - (a) V.B.theory
- (b) Hybridisation
- (c) M.O.theory
- (d) VSEPR theory
- 3. Maximum number of electrons that can be present in any molecular orbital is
 - (a)3
- (b) 6
- (c) 8
- (d)2
- 4. Which molecule/ion out of the following does not contain unpaired electrons?
 - (a) N_2^+
- (b) O_2
- (c) O_2^{2-}
- (d) B_2
- 5. Which of the following cannot be formed?

 - (a) He^{2+} (b) He+
- (c) He
- (d) *He*₂
- **6.** A bonding molecular orbital is produced by
 - (a) Destructive interference of wave functions
 - (b) Constructive interference of wave functions

 - (c) Pairing of electrons with opposite spins
- (d) Combination of +ve and –ve wave functions 7. Which of the following statements is not correct regarding bonding molecular orbitals?
 - (a) Bonding molecular orbitals possess less energy than the atomic orbitals from which they are
 - (b) Bonding molecular orbitals have low electron density between the two nuclei.
 - (c) Electron in bonding molecular contibutes to the attraction between atoms.

- (d) They are formed when the lobes of the combining atomic orbitals have the same sign.
- 8. The wavelength of the wave function of a bonding molecular orbital formed by LCAO is
 - (a) Equal to the wave function of atomic orbital
 - (b) Less than the wave function of atomic orbital
 - (c) Greater than the wave function of atomic orbital
 - (d) Double the wave function of atomic orbital
- 9. Which of the following order of energies of molecular orbitals of N₂ is correct?

(a)
$$(\pi 2 p_y) < (\sigma 2 p_z) < (\pi^* 2 p_x) \approx (\pi^* 2 p_y)$$

(b)
$$(\pi 2 p_y) > (\sigma 2 p_z) > (\pi^* 2 p_x) \approx (\pi^* 2 p_y)$$

(c)
$$(\pi 2 p_y) < (\sigma 2 p_z) > (\pi^* 2 p_x) \approx (\pi^* 2 p_y)$$

(d)
$$(\pi 2 p_y) > (\sigma 2 p_z) < (\pi^* 2 p_y) \approx (\pi^* 2 p_y)$$

10. Which one is paramagnetic and has a bond order

of
$$\frac{1}{2}$$
?

- (a) O_2^- (b) N_2^+ (c) F_2 (d) H_2^+
- 11. Which of the following options represents the correct bond order?
 - (a) $O_2^- > O_2^+ > O_2^+$
- (b) $O_2^- < O_2 < O_2^+$
- (c) $O_2^- > O_2 < O_2^+$
- (d) $O_2^- < O_2 > O_2^+$
- 12. In which pair, the stronger bond found in the first species
 - (I) O_2^-, O_2 (II) N_2, N_2^+ (III) NO^+, NO^-
 - (a) (I) only
- (b) (II) only
- (c) (I) and (III) only
- (d) (II) and (III) only

- 13. The bond length of H_2^+, H_2^- and H_2 are in the

 - (a) $H_2^+ > H_2 > H_2^-$ (b) $H_2 > H_2^+ > H_2^-$
 - (c) $H_2^- > H_2^+ > H_2^+$ (d) $H_2^- > H_2^+ > H_2^+$
- 14. Which of the following statement is not correct from the view point of molecular orbital theory? (a) Be, is not a stable molecule.
 - (b) He₂ is not stable but He_2^+ is expected to exist.
 - (c) Bond strength of N, is maximum amongst the homonuclear diatomic molecules belonging to the second period.
 - (d) The order of energies of molecular orbitals in N, molecule is

$$\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

15. Which of the following statement is correct about

 N_2 molecule?

- (a) It has a bond order of 3
- (b) The number of unpaired electrons present in it is zero and hence it is diamagnetic
- (c) The order of filling of MOs is

$$\pi(2p_x) = \pi(2p_y), \sigma(2p_z)$$

- (d) All statements are correct
- **16.** The electron probability density Ψ_{RMO}^2 is higher than the sum for individual atomic orbitals $(\Psi_A^2 + \Psi_B^2)$ by a factor of
- (a) $2\Psi_A$ (b) $2\Psi_B$ (c) $2\Psi_A\Psi_B$ (d) $\Psi_A^2\Psi_B^2$
- 17. Among the following the one that has two nodal planes is
 - (a) σ_{nn}^* (b) σ_{nn}^* (c) σ_{2n}^* (d) σ_{2n}

- 18. The incorrect statement among the following is
 - (a) In C_2 , there is a double bond and both the bonds are π – bonds
 - (b) Bond order of CO and CO^+ are respectively 3.0 and 3.5
 - (c) CO, NO^+ and N_2 all have the same bond order value
 - (d) The B.O of CO = 2, $NO^+ = 2.5 \& N_2 = 3$
- 19. Four diatomic species are listed below in different sequences. The correct order of their bond orders is

- (a) $C_2^{2-} < He_2^+ < NO < O_2^{-}$
- (b) $He_2^+ < O_2^- < NO < C_2^{2-}$
- (c) $O_2^- < NO < C_2^{2-} < He_2^+$
- (d) $NO < C_2^{2-} < O_2^{-} < He_2^{+}$
- 20. The diagram shows:

- (a) σ_{nc} (b) σ_{nc}^* (c) σ_{nD} (d) σ_{nD}^*
- 21. The decreasing order of bond length for N2 and its ions is correctly shown in
 - (a) $N_2 > N_2^- = N_2^+ > N_2^{2-} = N_2^{2+}$
 - (b) $N_2^{2-} = N_2^{2+} > N_2^{-} = N_2^{+} > N_2$
 - (c) $N_2^{2-} > N_2^{1+} > N_2^{-} > N_2^{2+} > N_2$
 - (d) $N_2^{2-} > N_2^- > N_2 > N_2^+ > N_2^{2+}$
- 22. O_2 and N_2 if converted to O_2^+ and N_2^+ respectively. The incorrect statement is
 - (a) Electron in O_2 goes form π_{2n}^*
 - (b) Electron in N_2 goes from σ_{2p_2}
 - (c) Bond length Q Q > bond length $(Q Q)^+$
 - (d) Bond length N N > bond length $(N N)^+$
- 23. The common features among the species

CN[−].CO and NO⁺ are

- (a) bond order three and isoelectronic
- (b) bond order three and weak field ligands
- (c) bond order two and π acceptors
- (d) isoelectronic and weak field ligands
- 24. What is the effect of the following processes on the bond order in N₂ and O₂?
 - i) $N_2 \to N_2^+ + e^-$ ii) $O_2 \to O_2^+ + e^-$
 - (a) Decreases in both (i) & (ii)
 - (b) Increases in both (i) & (ii)
 - (c) Increases in (i) but decreases in (ii)
 - (d) Decreases in (i) but increases in (ii)
- 25. In which set of molecules all the species are paramagnetic?
 - (a) B_{2}, O_{2}, N_{3}
- (b) B_2, O_2, NO
- (c) B_{2}, F_{2}, O_{2}
- (d) B_{2}, O_{2}, Li_{3}

- **26.** A mong KO_2 , AlO_2^- , BaO_2 and NO_2^+ , unpaired electron is present in
 - (a) NO_2^+ and BaO_2^-
- (b) KO_2 and AlO_2^-
- (c) KO₂ only
- (d) BaO_2 only
- 27. A molecule may be represented by three structures having energies E_1, E_2 and E_3 respectively. The energies of these structures follow the order $E_3 < E_2 < E_1$ respectively. If the experimental energy of the molecule is E_0 , the resonance energy is
 - (a) $(E_1 + E_2 + E_3) E_0$ (b) $E_0 E_3$
 - (c) $E_0 E_1$ (d) $E_0 E_2$

ANSWER KEY

1. c	2. c	3. d	4. c	5. d
6. b	7. b	8. a	9. a	10. d
11. b	12. d	13. d	14. d	15. d
16. c	17. c	18. d	19. b	20. d
21. b	22. d	23. a	24. d	25. b
26. c	27. b			

HINTS & SOLUTIONS

3.Sol: According to Pauli's exclusion principle. **5.Sol:** He, cannot be formed because bond order is zero.

- 7.Sol: Bonding M.O. has maximum electron density between two nuclei.
- B.O. 10.Sol: Ions 1.5 2.5 1 0.5
- 11.Sol: Ions B.O. 1.5 2 2.5
- 12.Sol: B.O. is directly proportional to the strength of the bond.
- 13.Sol: Higher is the B.O. lower is the bond length.
- 17.Sol: ABMO p, have two nodal planes
- **19.Sol:** Bond orders are : $He_2^+ = 0.5$; $O_2^- = 1.5$;

$$NO = 2.5; C_2^{2-} = 3.0$$

- **21.Sol:** Bond order of N_2^{2-} and N_2^{2+} is 2
 - Bond order of N_2^- and N_2^+ is 2.5

Bond order of N_2 is 3.

- 23.Sol: CN^- , CO and NO^+ are Isoelectronic $(14\overline{e})$ and has bond order 3.
- **26.Sol:** KO_2 has K^+ and O_2^- structure having one un paired electron.
- **27.Sol:** The difference in energy of the actual molecule (experimental value) and energy of the most stable resonating structure is called resonance energy.

MOCK TEST PAPER

NEET - 5

2018

- 1. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of given atomic species?
 - (a) F < Cl < O < S
 - (b) S < O < Cl < F
 - (c) O < S < F < C1
 - (d) Cl < F < S < O
- 2. The pair of amphoteric hydroxides is
 - (a) $Al(OH)_{2}$, LiOH
 - (b) $Be(OH)_{2}$, $Mg(OH)_{2}$
 - (c) $B(OH)_2$, $Be(OH)_2$
 - (d) $Be(OH)_{2}$, $Zn(OH)_{2}$
- 3. The dipole moment of o,p and m-dichlorobenzene will be in the order
 - (a) o > p > m
- (b) p > o > m
- (c) m > o > p
- (d) o > m > p
- 4. Between any two of the following molecules, hydrogen bonding is not possible
 - (a) Two primary amine molecules
 - (b) Two secondary amine molecules
 - (c) Two tertiary amine molecules
 - (d) Two ammonia molecules
- 5. The common features among the species CN[−].CO and NO⁺ are
 - (a) Bond order three and isoelectronic
 - (b) Bond order three and weak field ligands
 - (c) Bond order two and π acceptors
 - (d) Isoelectronic and weak field ligands
- **6.** Equal number of moles of CO and CO₂ are filled in a chamber at room temperature. The correct relationship w.r.t their partial pressure P_{CO} and P_{CO_2} is

- (a) $P_{CO} > P_{CO}$
- (b) $P_{CO} < P_{CO}$
- (c) $P_{CO} = P_{CO_2}$
- (d) zero
- 7. The average speed at temperature $T \circ C$ of $CH_4(g)$

is
$$\sqrt{\frac{28}{88}} \times 10^3 \, ms^{-1}$$
. What is the value of T?

- (a) 24055°C
- (b) $-32.45^{\circ}C$
- (c) $3000^{\circ}C$
- (d) $-24.055^{\circ}C$
- 8. Which of the following behaviour is true regarding the coefficient of viscosity (η) of a liquid?
 - (a) Plot of η versus T is non linear
 - (b) Plot of η versus $\frac{1}{\tau}$ is linear
 - (c) $\eta = \frac{E}{RT}$
 - (d) Plot of log η versus $\frac{1}{T}$ is non linear
- 9. Ionic product of water at 310 K is 2.7×10^{-14} . What is the pH of neutral water at this temperature? (c)6.3(a) 7 (b) 7.3 (d) 6.8
- **10.** The solubility of $Ca(OH)_2$ is $\sqrt{3}$. The solubility product of Ca(OH), is
 - (a) 3
- (b) 27
- (c) $\sqrt{3}$ (d) $12\sqrt{3}$
- 11. In the reaction:

$$CS_{2(I)} + 3O_{2(g)} \rightarrow CO_{2(g)} + 2SO_{2(g)}; \Delta H = -265 \text{ kcal}$$

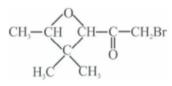
The enthalpies of formation for both CO, and SO, are negative and are in the ratio 4:3. The enthalpy of formation for CS, is + 26 kcal/mol. The enthalpy

of formation for SO, is

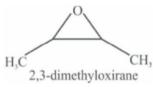
- (a) -90 kcal/mol
- (b) -52 kcal/mol
- (c) -78 kcal/mol
- (d) -71.7 kcal/mol
- 12. Consider the following reaction between zinc and oxygen and choose the correct options out of the options given below:
 - (a) The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.
 - (b) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.
 - (c) 598.3 kJ mol⁻¹ energy is evolved in the reaction.
 - (d) 693.8 kJ mol⁻¹ energy is absorbed in the reaction.

The common name of given ester is

- (a) Neo butyl iso butyrate
- (b) t-Butyl n- butyrate
- (c) t- Butyl iso butyrate
- (d) iso butyl iso butyrate
- 14. IUPAC name of the following compound is



- (a) 1-Bromo-3,5-epoxy-4,4-dimethyl-2- hexanone
- (b) 1-Bromo-3,3-dimethyl-2-oxo-2-hexanone
- (c) 1-Bromo-3,3-dimethyl acetone
- (d) 1-Bromo-4,4-dimethyl-5-oxo-hexanone
- 15. How many geometrical isomers possible for the compound?



- (a) 0
- (b) 2
- (c) 3
- 16. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment?
 - (a) $3d^{7}$
- (b) $3d^{5}$
- (c) $3d^{8}$
- (d) $3d^{2}$

- 17. Railway wagon axles are made by heating rods of iron embedded in charcoal powder. The process is known as
 - (a) Case hardening
- (b) Sherardising
- (c) Annealing
- (d) Tempering
- 18. Gun metal contains
 - (a) Cu, Sn, Zn
- (b) Cu, Ni
- (c) Cu, Ni, Fe
- (d) Cu. Sn. P



Product (is

- (a) Vinyl chloride
- (b) Vinyl iodide
- (c) Allyl chloride
- (d) Allyl iodide
- 20. What amount of bromine will be required to convert 2g of phenol into 2,4,6-tribromophenol?
 - (a) 10.22
- (b) 20.44
- (c)4.00
- (d)6.00
- **21.** Which is lyophobic in nature?
 - (a) Gelatin (c) Starch
- (b) Phosphorus (d) Agar-Agar
- 22. Which of the following is not a gel?
 - (a) Cheese (b) Jelly
- (c) Curd (d) Milk
- 23. Conductance of 0.1 M KCl (conductivity = X ohm ¹ cm⁻¹) filled in a conductivity cell is Y ohm⁻¹. If the conductance of 0.1 M NaOH filled in the same cell is Z ohm⁻¹, the molar conductance of NaOH will be
 - (a) $10^3 XZ/Y$
- (b) $10^4 XZ/Y$
- (c) 10 XZ/Y
- (d) 0.1 XZ/Y
- 24. In the button cell widely used in watches and other devices the following reaction takes place:

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^{-}_{(aq)}$$

Determine $\Delta_{\cdot}G^{\circ}$ for the reaction.

(Given $E_{cell}^o = 1.11 \text{ V}$)

- (a) $-2.14 \times 10^4 \text{ J}$
- (b) $-2.14 \times 10^4 \text{kJ}$
- (c) 214 kJ
- (d) 214 J
- **25.** For a first order reaction $A \rightarrow B$ the reaction rate at which reactant concentration of 0.01 M is found to be 2.0×10^{-5} M sec⁻¹. The half-life period of the reaction is:
 - (a) 30 s(b) $300 \, s$
- (c) $220 \, s$
- (d) 347s.
- 26. Two substances A and B are present such that $[A]_0 = 4[B]_0$ and half life of A is 5 minute and that of B is 15 minute. If they start decaying at the same time following first order kinetics how much time will the concentration of both of them would be

the same?

- (a) 15 minute
- (b) 10 minute
- (c) 5 minute
- (d) 12 minute
- 27. M=molarity of the solution m=molality of the solution

d=density of the solution (in g. ml^{-1})

 $M^1 = \text{gram molecular weight of solute}$ Which of the following relations is correct?

(a)
$$m = \frac{M}{1000d - MM^1}$$

(b)
$$m = \frac{M \times 1000}{d + MM^{1}}$$

(c)
$$m = \frac{M \times 1000}{(1000 \times d) - MM^1}$$

(d)
$$M = \frac{m \times 1000}{(1000 \times d) - MM^1}$$

28. X is non volatile solute and Y is a volatile solvent. Following V.P. are observed by dissolving X in Y.

X(M)0.10

- 0.25 0.01 P,
- Y (mm of Hg) (a) $P_1 < P_2 < P_3$
- (c) $P_3 < P_1 < P_2$
- (b) $P_3^2 < P_2 < P_1^3$ (d) $P_2 < P_1 < P_3^3$
- 29. Equimolal solutions of potassiumhexacyanoferrate (II), (represented as X) and potassium hexacyanoferrate (III), (represented as Y) are considered, which are at equal degree of dissociation. Which of the following statement is correct?
 - (a) The boiling point of X is greater than Y.
 - (b) X and Y have the same boiling point.
 - (c) The boiling point of X is less than Y.
 - (d) X and Y have the same freezing point.
- **30.** The spin only magnetic moment of [MnBr₄]²⁻ is 5.9BM. The geometry of the complex ion is
 - (a) Tetrahedral
- (b) Square planar
- (c) Pyramidal
- (d) Octahedral
- 31. Which of the following complexes exhibit optical isomerism?
 - (a) Trans-tetraamminedithiocyanatochromium (III)
 - (b) Cis-diamminedicarbonatacobaltate (III) ion
 - (c) Trans-diamminedicarbonatacobaltate (III) ion
 - (d) Cis-bis (glycinato) platinum (II)

32. The bond length of C-O bond in carbon

monoxide is 1.28 $\stackrel{\circ}{A}$. The C-Q bond in $Fe(CO)_5$

- (a) 1.15 A (b) 1.128 A (c) 1.118 A (d) 1.72 A
- 33. D-Glucose reacts with phenylhydrazine to make osazone. How many molecules of phenylhydrazine are used for this reaction per molecule of D-glucose
 - (a) One
- (b) Two
- (c) Three
- (d) Four
- 34. Amino acids exist in zwitter ion form. What is the structure of glycine at pH = 4?
 - (a) H_3N^{\oplus} CH_2 COO^{-1}
 - (b) $H_3N^{\oplus} CH_2 COOH$
 - (c) $H_2N CH_2 COOH$
 - (d) $H_2N CH_2 COO^{-1}$
- 35. The proteins with a prosthetic group are called
 - (a) Pseudo proteins
- (b) Complex proteins
- (c) Polypeptides
- (d) Conjugated proteins
- **36.** Compounds X and Y are obtained by the reaction of Cl, with cold and dilute solution of NaOH and compounds X and Z are formed with hot and concentrated solution of NaOH.

The compounds Y and Z respectively are

- (a) NaCl, NaClO
- (b) NaClO, NaClO,
- (c) NaCl, NaClO,
- (d) NaClO, HCl
- 37. By adding gypsum to cement
 - (a) setting time of cement becomes less.
 - (b) setting time of cement increases.
 - (c) colour of cement becomes light.
 - (d) shining surface is obtained.
- 38. In the carbon family the melting points of the elements decrease on descending the group because the interatomic bonds become:
 - (a) Stronger as the size of the atom increases
 - (b) Weaker as the size of the atom decreases
 - (c) Stronger as the size of the atom decreases
 - (d) Weaker as the size of the atom increases
- 39. Carbogen is
 - (a) Mixture of $90-95\% O_2 + 5-10\% CO_2$
 - (b) Used by pneumonia patients for respiration
 - (c) Used by victims of CO for respiration
 - (d) All of these
- 40. Pyrex glass is a mixture of

- (a) sodium borosilicate and barium borosilicate
- (b) sodium silicate and calcium silicate
- (c) sodium silicate and lead silicate
- (d) sodium silicate and aluminium borosilicate
- **41.** The number of cis-trans isomers with molecular formula $C_2BrClFI$ is
 - (a) 4
- (b) 6
- (c)7
- (d) 8
- **42.** A compound (X) when passed through dil. H_2SO_4 gives compound (Y), which on reaction with HI and red phosphorous gives C_2H_6 . The compound (X) is
 - (a) Ethane
- (b) Ethyne
- (c) 2-Butene
- (d) 2-Butyne
- **43.** In the reaction of p-chlorotoluene with KNH_2 in liquid NH_3 , the major product is
 - (a) o-Toluidine
- (b) m-Toluidine
- (c) p-Toluidine
- (d) p-Chloroaniline
- **44.** Aniline on treatment with sodium hypochlorite gives
 - (a) p-aminophenol
- (b) phenol
- (c) sodium salt of aniline (d) anilinium chloride
- **45.** The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is
 - (a) methylamine
- (b) ethylamine
- (c) diethylamine
- (d) triethylamine

ANSWER KEY

3. d 1. c **2.** d 4. c **5.** a 6. c **7.** b **8.** a **9.** d 10. d 11. d 12. a 13. c **14.** a 15. b **16.** b **17.** a 18. c 19. c **20.** a **21.** b 22. d 23. b 24. c 25. d **30.** a **26.** a **27.** c 28. d **29.** a **31.** b **32.** d **33.** c **34.** b 35. d **37.** b **39.** d **36.** b **38.** d **40.** a **41.** b **42.** b **43.** b **44.** a **45.** c

HINTS & SOLUTIONS

- **3.Sol:** Bond angle increases dipole moment decreases.
- **5.Sol:** CN^- , CO and NO^+ are Isoelectronic $(14\overline{e})$

and has bond order 3.

6.Sol: They are non-reacting gases.

7.Sol:
$$\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{28}{88}} = \sqrt{\frac{7}{22}}$$

$$\frac{8 \times 8.314 \times T}{\pi \times 16 \times 10^{-3}} = \frac{7}{22} \times 10^{6}$$

$$T = \frac{1000 \times 2}{8.314} = 240.55K$$

$$T^{\circ}C = 240.55 - 273 = -32.45^{\circ}C$$

9.Sol:
$$K_w = [H_3O^+] \cdot [OH^-] = 2.7 \times 10^{-14} \text{ at } 310 \text{K}$$

 $H_2O + H_2O \rightleftharpoons [H_3O^+] [OH^-]$

$$\left[\!\!\left[H_3O^+ \right] \!\!\right] \!=\! \left[OH^- \right]$$

Therefore,

$$[H_3O^+] = \sqrt{2.7 \times 10^{-14}} = 1.643 \times 10^{-7} M$$

$$pH = -\log[H_3O^+] = -\log 1.643 \times 10^{-7}$$

$$pH = 7 + (-0.2156) = 6.7844.$$

10.Sol:
$$Ca(OH)_2 \rightleftharpoons Ca_s^{2+} + 2OH_{2s}^{-}$$

$$K_{sp} = (s)(2s)^2 = 4s^2, s = \sqrt{3}$$

$$K_{sp} = 4(\sqrt{3})^3 = 12\sqrt{3}$$

11.Sol:
$$CS_{2(1)} + 3O_{2(g)} \rightarrow CO_{2(g)} + 2SO_{(g)}$$

 $\Delta H = -265 \text{ kcal}$

$$\Delta H_f^o(CO_2, g)=4x$$

$$\Delta H_f^o(SO_2, g) = 3x$$

$$\Delta_{\rm r}H = \sum \Delta_{\rm f}H^o_{\rm products} - \sum \Delta_{\rm f}H^o_{\rm reactants}$$

$$-265 = 4x + 6x - 26$$

$$10x = 239$$

$$x = -23.9$$

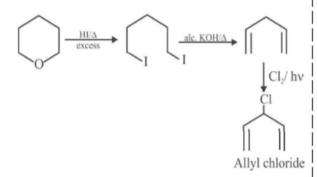
$$\Delta H_f^o(SO_2, g) = -71.7 \text{ kcal/mol}$$

13.Sol: Iso-octane is

17.Sol: Case hardening: The process of hardening the surface of wrought iron by depositing a surface layer of steel on it is called case-hardening. It is done by heating wrought iron in contact with potassium ferrocyanide.

Alternatively, case hardening can also be done by heating wrought iron with charcoal and then plunging it a suitable oil.

19.Sol:



94 g of phenol reacts with 480 g of Br_2 .

2 g of phenol reacts with $\frac{480}{94} \times 2 = 10.22g$ of

 Br_2 .

23.Sol: Conductivity $(X) = \text{conductance} \times \text{cell}$ constant

> Cell constant = X/YConductivity of NaOH = XZ/Y Λ_m (NaOH) = 10^4 XZ/Y

24.Sol: NH, produced due to cathodic reaction,

 $MnO_2 + NH_4^+ + e \rightarrow MnO(OH) + NH_3$ combines

With Zn^{2+} to form $Zn(NH_3)_4^{2+}$

rate = $k[A]^1$ **25.Sol:** $k = \frac{2.0 \times 10^{-5}}{0.01} = 2.0 \times 10^{-3}$

$$\therefore t_{\frac{1}{2}} = \frac{0.693}{2.0 \times 10^{-3}} = 347 \text{ s}$$

- 28.Sol: Amount of solute or concentration of the solute increases vapour pressure of volatile solvent decreases.
- **30.Sol:** Since the coordination number of Mn²⁺ ion in the complex ion is 4, it will be either tetrahedral (sp³) hybridisation) or square planar (dsp²hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the d-orbitals.

(Note: CO_3^{2-} acts as bidented in this complex)

32.Sol: Due to synergic bond formation, bond order decreases and bond length increases a little.

35.Sol: Simple protein and Prosthetic group (nonprotein material gives conjugated proteins.

36.Sol:
$$Cl_2 + 2NaOH \rightarrow 2NaCl + NaClO + H_2O$$

(cold dil.) (X) (Y)
 $3Cl_2 + 6NaOH(hot) \rightarrow 5NaCl + NaClO_3 + 3H_2O$.
(X) (Y)

41.Sol: Six isomers are:

42.Sol: The compound (X) is likely to be alkyne which | **43.Sol:** reacts with water in the presence of H_2SO_4 and

 $HgSO_4$ as catalyst to form a carbonyl compound. HI and red phosphorous can reduce a carbonyl compound to alkane having same number of carbon atoms.

Therefore (Y) is likely to be acetaldehyde, which is the hydration product of ethyne.

$$\begin{split} HC &\equiv CH + H_2O \xrightarrow{H_2SO_4} \left[CH_2 = CH - OH \right] \\ &(X) \\ &\rightleftharpoons CH_3 - CHO \\ &(Y) \\ CH_3CHO + 4HI \xrightarrow{\text{red P}} CH_3CH_3 + 2I_2 + H_2O \end{split}$$

Therefore, (X) is ethyne.

This reaction proceeds through benzyne mechanism.

45.Sol: 2° amine.





7. EQUILIBRIUM

(1) Chemical equilibrium

- At equilibrium, rate of forward reactions is equal to the rate of backward reaction.
- At equilibrium, concentration of reactant and products remains constant.
- **O** At equilibrium, state $\Delta G = 0$.
- (2) Equilibrium Constant (K)

$$aA_{(g)} + bB_{(g)} \mathop{\Longrightarrow}\limits_{} cC_{(g)} + dD_{(g)}$$

$$\frac{k_{f}}{k_{b}} = K = \frac{\left[C\right]^{c}\left[D\right]^{d}}{\left[A\right]^{a}\left[B\right]^{b}}$$

(3) Relationship between K_p and K_c

$$\mathbf{K}_{P} = \mathbf{K}_{C} \times (\mathbf{R}\mathbf{T})^{\Delta n}$$
$$\Delta n = (c + d) - (a + b)$$

(4) Expressions for K_c and K_p for some reactions

Reaction	K _c	K_p
$mR \rightleftharpoons qP$	$\frac{\left(n_{P}\right)^{q}}{\left(n_{R}\right)^{m}}V^{\Delta n}$	$\frac{\left(n_{P}\right)^{q}}{\left(n_{R}\right)^{m}} \left[\frac{P}{\sum n}\right]^{\Delta n}$
$H_2(g)+I_2 \Longrightarrow 2HI(g)$	$\frac{4x^2}{(a-x)(b-x)}$	$\frac{4x^2}{(a-x)(b-x)}$
$N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g)$	$\frac{4x^2V^2}{(a-x)(b-3x)^3}$	$\frac{4x^2}{P^2(a-x)(b-3x)^3}$
$PCl_5(g) \Longrightarrow PCl_3(g) + Cl_2(g)$	$\frac{x^2}{(1-x)V}$	$\frac{x^2P}{\left(1-x^2\right)}$
$N_2O_4(g) \Longrightarrow 2NO_2(g)$	$\frac{4x^2}{(1-x)V}$	$\frac{4x^2P}{\left(1-x^2\right)}$
$CaCO_3(s) \Longrightarrow CaO(s) + CO_2(g)$	[CO ₂]	P_{CO_2}

Where, a and b are the initial concetrations of two reactants, and 'x' is the extent of reaction. $\Sigma n = \text{Total number of moles at equilibrium and P is the total pressure.}$

(5) Factors influencing equilibrium constant, K

- O Equilibrium constant depends on
- (I) Temperature

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 - T_2} \right]$$

- (II) Mode of writing the equation
- For the reactions,

$$A \rightleftharpoons B$$
 $B \rightleftharpoons A$

if $K_c = K$ then $K_c = 1/K$

(III) Stoichiometric coefficients

$$A \longrightarrow B$$
 $2A \longrightarrow 2B$ $\frac{1}{2}A \longrightarrow \frac{1}{2}B$
if $K_c = K$ then $K_c = K^2$ & $K_c = \sqrt{K}$

$$O A \longrightarrow B$$
 $B \longrightarrow C$ $A \longrightarrow C$
if $K_c = K_1$ & $K_c = K_2$, then $K_c = K_1$. K_2

(6) Applications of equilibrium constant, K

- (I) Predicting the direction of the reaction If $Q_c > K_c$ Backward reaction is favoured. If $Q_c < K_c$ Forward reaction is favoured. If $Q_c = K_c$ Reaction mixture is at equilibrium.
- (II) Predicting the extent of a reaction If $K_c > 10^3$, products predominate over reactants, If $K_c > 10^{-3}$, reactants predominate over products, If K_c is in the range of 10^{-3} to 10^3 appreciable concentrations of both reactants and products are present.

(7) Le Chatelier prinicple

- (I) Effect of Concentration
- O If concentration of reactants is increased, the equilibrium shifts in forward direction.
- O If concentration of products is increased, the equilibrium shifts in backward direction.
- (II) Effect of Temperature
- Equilibrium will shift backward in exothermic and forward in endothermic when T is increased
- Equilibrium will shift forward in exothermic and backward in endothermic when T is decreased. (III) Effect of Pressure
- O Pressure change does not affect the gaseous reaction equilibrium where $\Delta n = 0$, i.e., $n_p = n_R$
- O But, when $n_P \neq n_R$, increase in pressure shifts | equilbrium in the direction of lower volume or

number of moles while decrease in pressure in the direction of higer volume or no. of moles.

- (IV) Addition of Catalyst
- Addition of catalyst lowers the activation energy of reaction. It increases rate of both forward and backward reactions to the same extent. Hence, equilbrium is not distrubed but is attained quickly.

(8) Relation between degree of dissociation and vapour density

$$\alpha = \frac{1}{n-1} \left\lceil \frac{D-d}{d} \right\rceil$$

$$\alpha = \frac{No.of\ moles\ dissociated}{Total\ No.of\ moles\ taken}$$

(9) Ionic equilibrium

Ostwald's Dilution Law

$$K_{eq} = \frac{C\alpha^2}{1-\alpha}$$
, for α weak electrolyte $1-\alpha \cong 1$

$$K_{_{eq}}=C\alpha^{^{2}},\alpha=\sqrt{\frac{K_{_{eq}}}{C}}$$

(10) Ionisation Constant of Water

 $K_w = [H^+][OH^-] \text{ or } K_w = [H_3O^+][OH^-]$

(11) pH scale

O
$$a_{n^+} = [H^+] mol.Lit^{-1}$$
.

O
$$pH = log_{10} \frac{1}{\lceil H^+ \rceil} \text{ (or) } [H^+] = 10^{-pH}$$

- \bigcirc pH + pOH = pK, at any temperature
- O At 25° C or 298K for any aqueous solution. pH + pOH = 14
- O At 25°C for pure water or neutral solution pH=pOH= 7.

(12) Calculation of pH of weak acids and weak bases

$$pH = -log[H^{+}]$$
 $pOH = -log[OH^{-}]$
= $-log_{10}[\sqrt{K_{a}C}]$ = $-log_{10}\sqrt{K_{b}C}$

(13) Salts Hydrolysis

O Salts of strong acids and strong bases do not undergo hydrolysis and the resulting solutions is neutral.

Salt	Hydrolysis	Resulting Solution	Hydrolysis constant (K_h)	Degree of hydrolysis (h)	рН
Weak acid and strong base	Anionic	Alkaline pH>7	$K_{h} = \frac{K_{w}}{K_{a}}$	$h = \sqrt{\frac{k_h}{C}}$	$pH = \frac{1}{2} \left[pK_w + pK_a + \log C \right]$
Strong acid and Weak base	Cationic	Acidic pH<7	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{k_h}{C}}$	$pH = \frac{1}{2} \left[pK_w - pK_b - \log C \right]$
Weak acid and Weak base	Anionic and cationic both	Neutral pH=7 (If $K_a = K_b$)	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{k_h}$	$pH = \frac{1}{2} \left[pK_{w} + pK_{a} - pK_{b} \right]$

(14) Buffer solutions

(I)Henderson - Hasselbalch equation

(i) pH of Acid Buffer

Mixture of CH, COOH + CH, COONa is an acid buffer.

$$pH = pK_{_a} + log \frac{[Salt]}{[Acid]}$$

(ii) pH of Basic Buffer

Mixture of NH₄OH + NH₄Cl is a basic buffer.

$$\Rightarrow$$
 pOH = pK_b + log $\frac{[Salt]}{[Base]}$

pH of buffer after adding H+ =

$$pK_{a} + log \frac{\left[Salt - x\right]}{\left[Acid + x\right]}$$

using AAA rule pH of buffer decreases.

(II) Buffer capacity or Buffer Index (ϕ)

The ability of the buffer to resist changes in pH.

(15) Solubility Product

 $A_{x}B_{y} \rightleftharpoons xA^{y+} + yB^{x-}$

$$K_{m} = [A^{y+}]^{x} [B^{x-}]^{y}$$

Let the solubility of A_vB_v is S then

$$K_{sp} = [xS]^{x} [yS]^{y} \Rightarrow K_{sp} = x^{x}.y^{y} [S^{x+y}]$$

$$S^{x+y} = \frac{K_{sp}}{x^x y^y} \quad \text{then} \quad S = x+y \frac{K_{sp}}{x^x y^y}$$

- O Ionic product and Solubility product
 - i)Ionic product = K_{SP} This is Saturated solution.
 - ii) Ionic product $< K_{SP}$ This means the solution is unsaturated and more salt can be dissolved
 - iii) Ionic product $> K_{SP}$ This means solution is holding more salt than it can dissolve in.

8. REDOX REACTIONS

(1) Oxidation and Reduction reactions

(I) Oxidant or oxidising agent Species, which oxidise other species, which is present in a reaction and reduce itself.

Some Important oxidising agent or oxidant

- All elements with high electronegative character like N, O, F, Cl, etc.
- All metallic oxides like Li,O, Na,O, Na,O,,CO,,CaO, MgO, BaO,
- OSome nonmetallic oxides like $CO_{2}, SO_{2}, H_{2}O_{2}, O_{3}$.

- All neutral compound or ion in which element shows their higher oxidation no. or state are act as oxidant or oxidising agent
- (II) Reductant or Reducing agent Species which reduce other element in a reaction and oxidise itself to donate electrons and show increase in its oxidation no. is called reductant or reducing agent.

Some Important reducing agents or reductants

- OAll metals like, K, Mg, Ca, etc.
- O All metallic hydrides like NaH, CaH_2 , $LiAlH_4$, $NaBH_4$, AlH_3 , etc.

- O All hydroacids like HF, HCl, HBr, H_2S etc.
- O Some organic compounds like aldehyde, formic acid, oxalic acid, tartaric acid.
- All neutral compounds or ions, which show their lower oxidation state.

(2) Oxidation number

- It represents the number of electron gained or lost by atom when it changes in compound from a free state.
- O Maximum oxidation no. of an element is equal to group no. in the periodic table
- O Minimum oxidation no. of an element is equal to group no. 8

(3) Oxidation state

Oxidation state of an atom is defined as oxidation number per atom for all practical purposes.

- O The rules to derive oxidation number or oxidation state are as follows
- O The O.S. of an element in its free state is zero. Example O.S.'s of Na, Cu, I_2 , Cl_2 , O_2 etc. are zero
- O Sum of O.S.'s of all the atoms in neutral molecule is zero.
- O Sum of O.S.'s of all the atoms in a complex ion is equal number of charge present on it.
- O In complex compounds, O.S. of some neutral molecules (ligands) is zero.

Example CO, NO, NH_3, H_2O .

- O Generally O.S. of oxygen is -2 but in H_2O_2 it is -1 and in O_2F_2 , it is +1, in OF_2 it is +2.
- Generally O.S. of Hydrogen is +1 but in metallic hydrides it is -1.
- O Generally O.S. of halogen atoms is −1 but in interhalogen compounds it changes.

(4) Redox Reactions

- (I) The reactions in which oxidation and reduction both occur simultaneously are called redox reactions.
- (II) Any redox reaction may be divided in two parts:
 - (i) Oxidation half reaction
 - (ii) Reduction half reaction

(5) Types of redox reactions

(I) Intermolecular redox reaction

$$2H_2 \overset{+6}{S} O_4(conc.) + \overset{0}{C} u \rightarrow Cu\overset{+2}{S} O_4 + \overset{+4}{S} O_2 + 2H_2O$$

(II) Intramolecular redox reaction

$$2K \overset{+5}{Cl} \overset{-2}{O_3} \rightarrow 2K \overset{-1}{Cl} + 3\overset{0}{O_2}$$

(III) Disproportion Redox Reaction
In this type of redox reactions same element acts as both oxidising & reducing agent.

$$\overset{0}{\text{Cl}_{2}} + \text{H}_{2}\text{O} \rightarrow \overset{+1}{\text{Cl}}\text{O} + \overset{-1}{\text{H}}\overset{-1}{\text{Cl}}$$

(6) Balancing redox reactions

(I) Half reaction method consider the example,

$$Cr_2O_7^{2-} + C_2O_4^{2-} \xrightarrow{H^+} Cr^{3+} + CO_2$$

(i) Write both the half reactions.

$$Cr_2O_7^{2-} \to Cr^{3+}$$
 (Reduction half reaction)

$$C_2O_4^{2-} \rightarrow CO_2$$
 (Oxidation half reaction)

(ii) Atoms other than H and O are balanced

$$Cr_2O_7^{2-} \to 2Cr^{3+}$$

$$C_2O_4^{2-} \rightarrow 2CO_2$$

(iii) Balance O-atoms by the addition of H_2O to another side

$$Cr_2O_7^{2-} \to 2Cr^{3+} + 7H_2O$$

$$C_2O_4^{2-} \rightarrow 2CO_2$$

(iv) Balance H-atoms by the addition of H^+ ions to another side

$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

$$C_2O_4^{2-} \rightarrow 2CO_2$$

(v) Now, balance the charge by the addition of electrons (e^{-}) .

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$C_2O_4^{2-} \to 2CO_2 + 2e^{-}$$

(vi) Multiply equations by a constant to get number of electrons same in both side. In the above case second equation is multiplied by 3 and then added to first equation.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$3C_2O_4^{2-} \rightarrow 6CO_2 + 6e^-$$

$$\overline{Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \to 2Cr^{3+} + 6CO_2 + 7H_2O}$$

In Alkaline medium

Consider the reaction

$$Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$$

- (i) Separate the two half reactions. $Cr(OH)_3 \rightarrow CrO_4^{2-}$ (Oxidation half reaction) $IO_3^- \rightarrow I^-$ (Reduction half reaction)
- (ii) Balance O- atoms by adding H_2O . $H_2O + Cr(OH)_2 \rightarrow CrO_4^{2-}$ $IO_3^- \rightarrow I^- + 3H_2O$
- (iii) Balance H-atoms by adding H_2O to side having deficiency and OH^- to other side having deficiency of H-atoms.

$$5OH^{-} + H_{2}O + Cr(OH)_{3} \rightarrow CrO_{4}^{2-} + 5H_{2}O \text{ or}$$

 $5OH^{-} + Cr(OH)_{3} \rightarrow CrO_{4}^{2-} + 4H_{2}O$
 $IO_{3}^{-} + 6H_{2}O \rightarrow I^{-} + 3H_{2}O + 6OH^{-} \text{ or}$
 $IO_{3}^{-} + 3H_{2}O \rightarrow I^{-} + 6OH^{-}$

- (iv) Balance the charges by electrons $5OH^{-} + Cr(OH)_{3} \rightarrow CrO_{4}^{2-} + 4H_{2}O + 3e^{-}$ $IO_{2}^{-} + 6H_{2}O + 6e^{-} \rightarrow I^{-} + 3H_{2}O + 6OH^{-}$
- (v) Multiply first equation by 2 and add to second to give

$$\begin{split} 10OH^{-} + 2Cr(OH)_{3} &\rightarrow 2CrO_{4}^{2-} + 8H_{2}O + 6e^{-} \\ IO_{3}^{-} + 6H_{2}O + 6e^{-} &\rightarrow I^{-} + 3H_{2}O + 6OH^{-} \\ 4OH^{-} + 2Cr(OH)_{3} + IO_{3}^{-} &\rightarrow 5H_{2}O + 2CrO_{4}^{2-} + I^{-} \end{split}$$

- (II) Oxidation number method
- (i) Write the skeleton equation (if not given, frame it) representing the chemical change.
- (ii) Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.
- (iii) Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.
- (iv) Complete the balancing by inspection. First balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally balance hydrogen and oxygen by putting H_2O molecules wherever needed.

The final balanced equation should be checked to ensure that there are as many atoms of each element on the right as they are on the left.

9. HYDEOGEN

(1) Hydrogen

- (I) Resemblance with alkali metals due to
- O Electronic configuration (ns^1) : $1s^1$ i.e., it has one electron in s - orbital of valence shell
- Oxidation state (+1): H^+Cl , Na^+Cl
- (II) Resemblance with halogens due to
- O Electronic configuration: One electron less than the nearest inert gas configuration
- Electronegative character: Both have tendency to accept one electron to form anions
- O Ionisation energy: Comparable with halogens. (III) Differences from alkali metals and halogens
- Less electropositive than alkali metals and less electronegative than halogens
- OSize of ions: H^+ is much smaller than alkali metal ions and H is much larger than halide ions.

- (2) Preparation of di hydrogen (H,)
- \bigcirc $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
- \bigcirc $CaH_2 + 2H_2O \xrightarrow{Fe_2O_3 \text{ or } Cr_2O_3} \rightarrow Ca(OH)_2 + 2H_2.$
- $O Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$
- \bigcirc 2Al + 2NaOH + 2H₂O \rightarrow 2NaAlO₂ + 3H₂

(Uveno's method)

- \bigcirc 3Fe+4H₂O \rightarrow Fe₃O₄+4H₂
- $O CO_{(g)} + H_2O_{(g)} \to CO_{2(g)} + H_{2(g)}$
- (3) Chemical Properties of dihydrogen
- $\bigcirc 2Na + H, \rightarrow 2NaH$
- O $H_2 + X_2 \rightarrow 2HX$
- O Reducing nature

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

Unsaturated fat $+H_2 \xrightarrow{Ni}$ Saturated fat (Oil) (Vanaspati Ghee)

(4) Different forms of H,

- (I) Nascent Hydrogen
- (II)Adsorbed Hydrogen
- (III)Atomic Hydrogen
- (IV)Ortho and Para hydrogen
 - (i) Ortho hydrogen: Spin of protons or nucleii are in same direction ortho hydrogen
 - (ii) Para hydrogen: Spin of protons or nucleii are in opposite direction.

(5) Hydrides

- (I) Ionic hydrides or Saline hydrides
- (II) Covalent hydrides or Molecular hydrides
- (III) Metallic or Interstitial hydrides
- (IV) Polymeric hydrides

(6) Hydrogen Peroxide

(I) Methods of preparation

$$BaO_2 + CO_2 + H_2O \rightarrow H_2O_2 + BaCO_3$$

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

By electrolysis of 50% H_2SO_4 at 0°C using Pt electrode.

$$2H_2SO_4 \rightarrow 2H^+ + 2HSO_4^-$$

At cathode (Cu):
$$2H^+ + 2e^- \rightarrow H_2$$

At anode (Pt):
$$2HSO_4^- \to H_2S_2O_8 + 2e^-$$

$$H_2S_2O_8 + 2H_2O \rightarrow H_2O_2 + 2H_2SO_4$$

2-Butylanthraquinone + H₂
$$\xrightarrow{PV}$$
 H₂O₂ + 2-Butyl anthraquinol Oxidation

- (II) Physical Properties
- O Pure H_2O_2 is weak acidic in nature and exists as associated liquid due to hydrogen bonding.
- \bigcirc Smell of H_2O_2 resembles like nitric acid.
- O It causes blisters on skin.
- O A dilute solution of H_2O_2 is concentrated by vacuum distillation or by distillation under pressure.
- (III) Chemical Properties

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

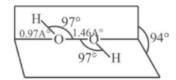
$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \rightarrow 2CrO_5 + K_2SO_4 + 5H_2O_1$$

$$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \rightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$$

(7) Strength of H_2O_2

Sample of H ₂ O ₂	% strength (w/v)	Molarity, M	Normality, N
5.6 vol. H ₂ O ₂	1.7% w/v	0.5 M	1 N
11.2 vol. H ₂ O ₂	3.4% w/v	1 M	2 N
22.4 vol. H ₂ O ₂	6.8% w/v	2 M	4 N
10 vol. H ₂ O ₂	3% w/v	0.89 M	1.78 N
100 vol. H ₂ O ₂	30% w/v	8.9 M	17.8 N

(8) Structure of H_2O_2



(9) Soft water and Hard water

- Water which gives foam easily with soap is known as soft water. The other which gives with difficulty is known as hard water.
- O Hardness of water is of two types
 - (I) Temporary hardness
 - (i) Due to soluble bicarbonates of Ca and Mg
 - (ii) It can be removed by boiling or adding

calculated quantity of slaked lime.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$

Clark's method

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

- (II) Permanent hardness
- O Due to soluble sulphates, chlorides, nitrates of Ca and Mg.
- O It can be removed
 - (i) By Permutit Process:
 - (ii) By washing soda (Na,CO₂):

$$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
(iii) Calgon's method:
Sodium hexametaphosphate
$$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+(M = Mg, Ca)$$
(iv) Synthetic resins method:
$$2RNa(s) + M^{2+}(aq) \rightarrow R_2M(s) + 2Na^+(aq)$$

$$2RH(s) + M^{2+}(aq) \Longrightarrow MR_2(s) + 2H^+(aq).$$

$$RNH_2(s) + H_2O(l) \Longrightarrow RNH_3^+.OH^-(s)$$

$$RNH_3^+.OH^-(s) + X^-(aq) \Longrightarrow RNH_3^+.X^-(s) + OH^-(aq)$$

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

10. S-BLOCK ELEMENTS (ALKALI & ALKALINE EARTH METALS)

(1) Alkali metals

• The elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr), constitute group 1 of the periodic table.

(2) Alkaline Earth Metals

O The elements of group 2 are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

(3) Atomic and Physical properties of s - block elements

Property	Alkali metal	Alkaline earth metal	
Atomic and Ionic radii	 The atoms of alkali metals have the largest size in their respective periods. The atomic radii increase on moving down the group among the alkali metals 	The atomic radii as well as ionic radii of the members of the family are smaller than the corresponding members of alkali metals.	
Ionisation Energy	1.P. of these metals decreases from Li to Cs	The I.P. values decreases with increase of atomic radii from Be to Ba	
Electronegativity	Electronegativity of alkali metals decreases down the group	Electronegativity decrease from Be to Ba	
Density	 Li is lightest known metal among all K is lighter than Na because of low density 	Density of Mg is greater than Ca	
Flame colour	 Characteristic flame colours are Li-crimson, Na-Golden yellow, K-pale violet, Rb and Cs-violet. 	Be and Mg do not show any colour as their electrons are more strongly bound. Ca-Brick red, Sr-Crimson	
		Ba-apple green	
Hydration of ions	 Smaller the cation greater is the degree of hydration. Hydration energy order is Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺ 		
Standard oxidation potential and reducing properties	Li have greatest reducing nature due to maximum hydration energy of Li ion	• Standard oxidation potentials are Be Mg Ca Sr 1.69 2.35 2.87 2.90	

(4) Chemical properties of s-block elements

Property	Alkali metal	Alkaline earth metal
Action with air	 They generally form oxides and peroxides. M+O₂ → M₂O → O₂ → M₂O₂ Peroxide 	They give oxides of ionic nature M ⁻² O ⁻² which are crystalline in nature.
Action with water	$2M + 2H_2O \longrightarrow 2MOH + H_2$	$M + 2H_2O \longrightarrow M(OH)_2 + H_2$
Hydrides	The tendency to form their hydrides decreases from Li to Cs, since the electropositive character decreases from Cs to Li.	The stability of hydrides decreases from Be to Ra
Carbonates and bicarbonates	$Li_{2}CO_{3} \longrightarrow Li_{2}O + CO_{2}$ $2MHCO_{3} \xrightarrow{300^{\circ}C} M_{2}CO_{3} + H_{2}O + CO_{2}$	$M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + CO_2 + \underset{(Solution)}{H_2O}$
Nitrates	$2MNO_3 \rightarrow 2MNO_2 + O_2 \text{ (except Li)}$ $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$	$M(NO_3)_2 \rightarrow MO + 2NO_2 + \frac{1}{2}O_2$
Solubilities in Liq NH ₃	Na \rightleftharpoons Na ⁺ (in Liq NH ₃)+e ⁻ (Ammoniated) M+(x+y)NH ₃ \rightarrow [M(NH ₃) _x] ⁺ +e ⁻ (NH ₃) _y (solvated electron)	 When such a solution is evaporated, hexammoniate, M(NH₃)₆ is formed.
Basic nature of hydroxide	LiOH < NaOH < KOH < RbOH < CsOH	Be(OH)2 < Mg(OH)2 $< Ca(OH)2 < Sr(OH)2$ $< Ba(OH)2$

and Magnesium

- O The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO_2 .
- \bigcirc Both LiCl and $MgCl_2$ are soluble in ethanol
- O Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, LiCl.2H₂O and MgCl₂.8H₂O

(5) Diagonal relationship between Lithium | (6) Diagonal relationship between Be and

O Compounds of Be like those of Al undergo hydrolysis.

$$BeCl_2 + 2H_2O \rightarrow Be(OH)_2 + 2HCl$$

 $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$

O Be forms complex anions (beryllates like aluminium forms aliminates, while other alkaline earth metals do not form complex anions.

$$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2 \uparrow$$

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \uparrow$$

O Beryllium and aluminium ions have strong tendency to form complexes BeF_4^{2-} , AlF_6^{3-} .

11. p-BLOCK ELEMENTS

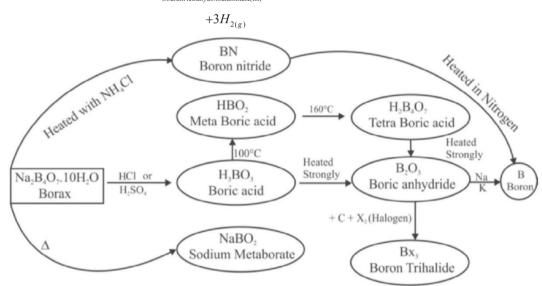
(1) Group - 13 elements

- O B, Al, Ga, In, and T*l* belongs to group 13 elements
- O General electronic configuration is ns²np¹
- Atomic radius increases suddenly from B to Al The atomic radii of Ga is less than Al. This is because of the poor shielding effect of d-electrons in Gallium.
- The order of ionization enthalpy is

- The common oxidation state of these elements is +3
- Amorphous boron and aluminium metal on heating in air form B₂O₂ and Al₂O₃ respectively.

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$

$$2\mathit{Al}_{(s)} + 2\mathit{NaOH}_{(aq)} + 6\mathit{H}_2\mathit{O}_{(l)} \rightarrow 2\mathit{Na}[\mathit{Al}(\mathit{OH})_4]_{(aq)}$$
 Sodium tetrahydoxoaluminate(III)



(2) Carbon family

- O Carbon, Silicon, Germanium, Tin and Lead are IV A group elements.
- The general outer electronic configuration of IV A group elements is $ns^2 np^2$.
- The number of electrons present in the penultimate shell of carbon is 2, Si is 8 while Ge, Sn, Pb contain 18 electrons each.
- O Covalent radius increases considerably from C to Si there after small increase is observed up to Pb due to completely filled d and f orbitals.
- O IP₁ & IP₂ order is C > Si > Ge > Pb > Sn
- The order of catenating power in IV A group elements is $C \gg Si > Ge > Sn > Pb$.

- O Common oxidation state of IV A group elements are +2, +4.
- When heated in oxygen form two types of oxides. Monoxide (MO) Dioxide (MO₂) C, Si, Ge are unaffected by water.
- O Sn reacts with steam to give SnO, and H,

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_{2(g)}$$

Pb is not affected by H_2O due to an oxide layer

onthe surface.

O Reaction with acids and base:

$$4Sn + 10HNO3 \rightarrow 4Sn(NO3)2 + NH4NO3 + 3H2O$$

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

Si + 2NaOH + H₂O
$$\rightarrow$$
 Na₂SiO₃ + 2H₂
Sodium Silicate

O The thermal stability of tetrahalides decreases in the order

$$CX_4 > Si X_4 > Ge X_4 > Sn X_4 > Pb X_4$$

Thermal stability order of hydrides:

$$CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$$

(3) Silicones

- Silicones are Organo Silicon polymers containing Si O Si bonds.
 - Polymerisation of dialkyl silane diols yield linear thermoplastic polymers.
- O Cyclic or ring silicones are formed when water is eliminated from terminal –OH groups of linear silicones.

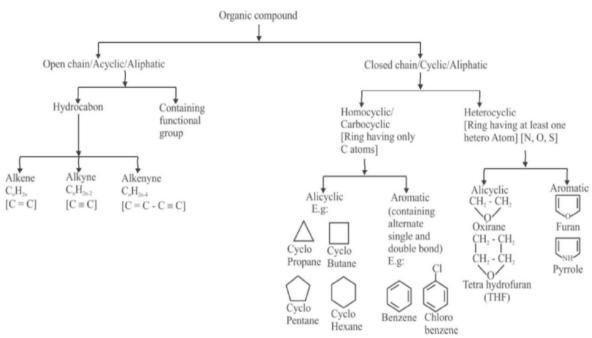
O Hydrolysis of RSiCl₃ gives crosslinked silicones. Commercial silicone polymers are usually methyl derivatives and to a lesser extent phenyl derivatives.

(4) Silicates

- O Silicates are the metal derivatives of silicic acid H_aSiO_a or $Si(OH)_a$.
- The basic structural unit in silicates is the SiO₄⁴, a tetrahedron.
- O Depending on the number of corners 0,1,2,3 or 4 of SiO₄⁴⁻ shared various kinds of silicates are formed

12. ORGANIC CHEMISTRY (SOME BASIC PRINCIPLES & TECHNIQUES)

(1) Classification of organic compounds



- A group of organic compounds which show similar properties but differ from the preceding or succeeding member by one -CH₂- (methylene) unit is known as Homologous series. The different members of a homologous series are called **homologues** and the phenomenon is called **homology**.
- (2) Nomenclature Of Organic Compounds
- O IUPAC nomenclature

Nomenclature according to IUPAC system involves use of following terms

2º Prefix+1º Prefix+ Root Word +1º Suffix+2º Suffix

(I) Root Word

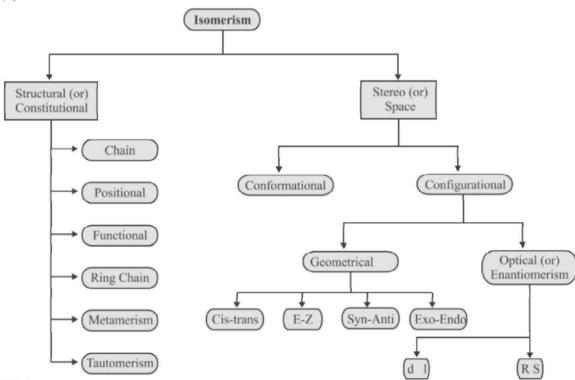
The root word represents the number of C atoms | in parent chain.

No. of C's	Root Word	No. of C's	Root Word
1	Meth	11	Undec
2	Eth	12	Dodec
3	Prop	13	Tridec
4	But	14	Tetradec
5	Pent	20	Eicos
6	Hex	30	Triacont
7	Hept	40	Tetracont
8	Oct	50	Pentacont
9	Non	60	Hexacont
10	Dec	100	Hect/Cent

(II) Suffix

GF & Common name	Suffix	IUPAC Name	Prefix
R-OH Alcohols	ol	Alkanol	Hydroxy
R-SH Thioalcohols	Thiol	Alkanethiol	Mercapto
R-NH ₂ Amines	Amine	Alkanamine	Amino
R-CHO Aldehydes	al	Alkanal	Formyl
RCO Ketones	one	Alkanone	Keto or oxo
RCOOH Carboxylic acids	oic acid	Alkanoic acid	Carboxy
RCONH2 Amides	amide	Alkanamide	Carbamoyl
RCOX Acid halides	oyl halide	Alkanoyl halide	haloformyl
RCOOR Esters	oate	Alkyl alkanoate	Carbalkoxy
RCN Nitriles	nitrile	Alkane nitrile	Cyano
RNC Isonitriles	isonitrile	Alkane isonitrile	Carbylamino

(3) Isomerism



(4) Fission or breaking of a covalent bond

The covalent bond is broken equally such that each of the bonded atoms retain their electron used in bonding. This leads to the formation of odd electron species known as **free radical**.

The covalent bond is broken unequally such that only one of the bonded atoms gets both the electrons resulting in the formation of positive and negative charged species.

(5) Attacking reagents

- I. Electrophiles or Electrophilic reagents.
- II. Nucleophiles or Nucleophilic reagents. atom has unfilled d-sub shells.

(6) Electron displacement effects in organic molecules

(I) Inductive effect:

The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect. The decreasing order of -I effect:

$$NR_3^+ > NH_3^+ > NO_2 > CN > SO_3H > COOH >$$

 $F > Cl > Br > I > OR > NR_2 > C_6H_5 > H$
 $(R = H, alkyl, aryl, acyl)$

The decreasing order of +I effect:

$$\dot{O} > -C_3 R_3 > -C_4 R_2 > -C_3 H_7 > -C_2 H_5 > -CH_3 > H$$

OApplications of Inductive Effect:

(i) Stability of carbonium ions:

The order of stability of carbonium ions is $3^{\circ} > 2^{\circ} > 1^{\circ} > Methyl$

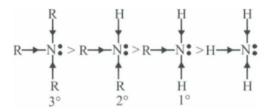
(ii)Stability of carbanions:

Methyl > 1° > 2° > 3°

(iii) Acidic strength of Carboxylic acids: EWG (-I) increases the acidic strength.

However, the EDG (+I) groups decrease the acidic strength.

(iv) Basicity of Amines: (+I) groups (EDG) increase the basic nature of amines, whereas (-I) groups (EWG) decrease the basic strength of amines.



(II) Electromeric effect:

The electronic system of an unsaturated molecule is deformed when the reagent approaches close to it. When the reagent is removed without allowing the reaction to takes place, the electronic system reverts to the original state of the molecule.

This kind of polarisation of multiple bonds is known as electromeric effect.

(III) Mesomeric effect:

Permanent polarisation in a compound due to delocalisation of π - e's along the conjugated systems caused by an atom or group in conjugation is called mesomeric effect

+M Effect atoms or groups

$$-NH_2$$
, $-NHR$, $-NR_2$, $-OH$, $-OR$, $-SR$, $-X(X = Cl, Br, I)$

(IV) Hyperconjugation or No bond resonance or Baker Nathan effect:

The delocalization of σ -electrons of C—H bond of an alkyl group into adjacent empty (or partially filled) non bonding p-orbital of carbon of a double bond or a carbocation or a free carbon radical is called hyperconjugation.

(7) Reaction intermediates

Property	Carbocation	Carbanion	Carbon free radical
Representation	\rightarrow C $_{\oplus}$	⇒č	>ċ
Bond fission	Heterolysis	Heterolysis	Homolysis
Electricity nature	Positive	Negative	Neutral
No. of electrons in valence shell	6	8	7
Hybridisation	sp^2	sp^3	sp ²
Shape	Planar	Pyramidal	Planar

(8) Purification of organic compounds

- (I) Sublimation
- The organic compounds such as benzoic acid, naphthalene, anthracene, camphor, indigo, anthraquinone etc., are purified by this process
- (II) Crystallisation
 - (i) Simple Crystallisation:
- O It is based on the fact that all organic compounds are more soluble in hot than in cold solvents, so that solid gets dissolved on heating and is obtained back on cooling.

E.g:

- O Sugar having an impurity of common salt can be crystallised from hot ethanol since sugar dissolves in hot ethanol but common salt does not.
 - (ii) Fractional Crystallisation:
- The process of separation of different components of a mixture by repeated crystallisation is called fractional crystallisation.
- Fractional crystallisation can be used to separate a mixture of KClO₂ (less soluble) and KCl (more soluble).

(III) Simple distillation:

O For example, chloroform (CHCl₂) and aniline

can be separated by simple distillation because of the large difference in their boiling points. Boiling point of (CHCl₂) is 60° and boiling point of aniline is 189°C. Ether (B.P. 308K) and toulene (B.P. 384K) can be separated by this method.

(IV) Fractional distillation

This method may be used to separate a mixture of acetone (b.p. 330K) and methyl alcohol (b.p. 338. K).

(V) Distillation under reduced pressure Certain liquids have a tendency to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation.

E.g. glycerol boils with decomposition at 563K

(VI) Steam distillation

Chromatography

- This technique is very useful for the separation, isolation, purification, and identification of the constituents of a mixture.
- (i) Adsorption Chromatography
- (A) Column Chromatography:
- (B) Thin layer chromatography:
- (ii) Partition chromatography

(9) Characterisation Of The Organic Compound Qualitative analysis (Detection of elements)

O Detection of Carbon and Hydrogen

Element	Detection	Confirmatory test	Reaction
Carbon	Copper (II) oxide test $2CuO + C \xrightarrow{\Delta} 2Cu + CO_2 \uparrow$	CO ₂ gas turns lime water milky	$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$ Lime water Milkiness
Hydrogen	$CuO + 2H \xrightarrow{\Delta} Cu + H_2O$	Water droplets appear on the cooler part of the ignition tube and also turns anhydrous CuSO ₄ blue.	$\begin{array}{c} CuSO_4 + 5H_2O \longrightarrow CuSO_4.5H_2O \\ \hline \text{While} \end{array}$

O Detection of Phosphorus

Element	Detection	Confirmatory test	Reaction
Phosphorus	$P \xrightarrow{Na_3O_3, boil} Na_3PO_4$	Solution is boiled with nitric acid and then treated with ammonium molybdate (NH ₄) ₂ MoO ₄ . Formation of yellow ppt. indicates the presence of phosphorus in organic compound.	$Na_3PO_4 + 3HNO_3 \longrightarrow$ $H_3PO_4 + 3NaNO_3$ $H_3PO_4 + 12(NH_4)_2MoO_4$ $+ 21HNO_3$ $\longrightarrow (NH_4)_3PO_4.12MoO_3$ Ammonium phosphomolybdate (yellow ppt) $+ 21NH_4NO_3 + 12H_2O$

O Detection of N, S and Halogens

N, S, and halogens present in an organic compound are detected by "Lassaigne's test".

Element	Detection	Confirmatory test	Reaction
Nitrogen	Lassaigne's extract (L.E.) $Na + C + N \xrightarrow{\Delta} NaCN_{(L.E.)}$	L.E. + FeSO ₄ + NaOH, boil and cool + FeCl ₃ + conc. HCl → blue or green colour.	FeSO ₄ + 2NaOH \longrightarrow Fe(OH) ₂ + Na ₂ SO ₄ Fe(OH) ₂ + 6NaCl \longrightarrow Na ₄ [Fe(CN) ₆] + 2NaOH 3Na ₄ [Fe(CN) ₆] + 4 FeCl ₃ \longrightarrow Fe ₄ [Fe(CN) ₆] ₃ + 12NaCl Prussian blue
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (L.E.)	 L.E. + sodium nitroprusside → deep violet colour L.E. + CH₃COOH	$Na_{2}S + Na_{2}[Fe(CN)_{3}NO] \longrightarrow$ Sodium nitroprusside $Na_{4}[Fe(CN)_{5}NOS]$ Deep violet $Na_{2}S + (CH_{3}COO)_{2}Pb \xrightarrow{CH,COOH}$ $PbS \downarrow + 2CH_{3}COONa$ Black ppt
Halogens	Na + X → NaX (I.E.)	L.E. + HNO ₃ + AgNO ₃ , if white ppt. soluble inaq. NH ₃ (or NH ₄ OH) confirms Cl dull yellow ppt. partially soluble in aq. NH ₃ (or NH ₄ OH) confirms Br. yellow ppt. insoluble in aq. NH ₃ (or NH ₄ OH) confirms I.	$NaX + AgNO_3 \xrightarrow{HNO_1} AgX \downarrow$ $AgCl + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]Cl$ White ppt $AgBr + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]Br$ Dull yellow ppt $Agl + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]l$ Yellow PPT $Ag(NH_3)_2[Ag(NH_3)_2]l$ Insoluble



Equilibrium

- 1. The reaction quotient (Q) predicts
 - (a) The direction of equilibrium to be attained
 - (b) The ratio of activities at equilibrium, i.e., K_C
 - (c) The ratio of activities at any time
 - (d) All of these
- 2. CH₃COOH₂⁺ is present in the solution of acetic acid in
 - (a) NH₃
- (b) Water
- (c) Benzene
- (d) HCl
- 3. When CO_2 is bubbled in excess of water, the following equilibrium is established.

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_2^-$$

$$K_a = 3.8 \times 10^{-7}, pH = 6$$

What would be the value of $[HCO_3^-]/[CO_2]$? (a) 6 (b) 0.0038 (c) 0.038 (d) 0.38

- **4.** The values of K_{p_1} and K_{p_2} for the reactions
 - $X \rightleftharpoons Y + Z$; $A \rightleftharpoons 2B$ are in the ratio 9:1. The total pressure at equilibrium are in the ratio, when the degree of dissociation of X and A are equal is (a) 36:1 (b) 1:1 (c) 3:1 (d) 1:9
- 5. The pH of blood is 7.4. Assuming that the buffer in blood is carbon dioxide, hydrogen carbonate ion, what is the ratio of conjugate base to acid necessary to maintain blood at its proper

(10) Quantitative Analysis [Estimation of elements]

Estimation of C & H

(Liebig's combustion method)

% of
$$C = \frac{12}{44} \times \frac{Mass \ of \ CO_2}{Mass \ of \ organic \ compound} \times 100$$

% of
$$H = \frac{2}{18} \times \frac{Mass \ of \ H_2O}{Mass \ of \ organic \ compound} \times 100$$

Estimation of Halogens (Carius Method)

$$X + AgNO_3 \longrightarrow AgX \downarrow$$

% of
$$Cl = \frac{35.5}{143.5} \times \frac{W_{AgCl}}{W_{Operation reported}} \times 100$$

% of
$$Br = \frac{80}{188} \times \frac{W_{AgBr}}{W_{O}} \times 100$$

% of
$$Br = \frac{80}{188} \times \frac{W_{AgBr}}{W_{Organic compound}} \times 100$$

% of $I = \frac{127}{235} \times \frac{W_{Agl}}{W_{Organic compound}} \times 100$

Estimation of Oxygen

% of O = 100 - (Sum of the % of all the elements in the compound) or

% of
$$O = \frac{16}{44} \times \frac{Mass\ of\ CO_2}{Mass\ of\ organic\ compound} \times 10^{-3}$$

pH? $(Ka = 4.5 \times 10^{-7})$

Redox Reactions

6. The reducing agent among the following is (a) HNO₂ (b) SO₂ (c) H₂S

(c) 11

(d) 12

7. Which of the following is not intramolecular redox reaction?

(a)
$$(NH_4)$$
, $Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

- (b) $2KClO_2 \longrightarrow 2KCl + 3O_2$
- (c) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$

(d)
$$2ClO_2 + 5H_2O_2 \xrightarrow{2OH^-} 2Cl^- + 5O_2 + 6H_2O$$

8. The position of some metals in the electrochemical series in decreasing electropositive character is given as Mg > Al > Zn > Cu > Ag. What will happen

Estimation of Nitrogen

Duma's Method:

$$C_xH_yN_z + (2x+y/2)CuO \longrightarrow xCO_2 + y/2H_2O + z/2 + N_2 + (2x+y/2)Cu$$

% of
$$N = \frac{28}{22400} \times \frac{V_{N_2} mL \text{ at STP}}{Wg} \times 100$$

Kjeldhal's Method:

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

 $2NH_3 + H_3SO_4 \longrightarrow (NH_4)_2SO_4$

% of
$$N = \frac{1.4 \times (NV)_{Acid used for NH_3}}{W}$$

Estimation of Sulphur (Carius Method)

$$S + HNO_3 \longrightarrow H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$$

% of
$$S = \frac{32}{233} \times \frac{Mass \ of \ BaSO_4}{Mass \ of \ compound} \times 100$$

Estimation of Phosphorous

% of
$$P = \frac{31}{1877} \times \frac{Mass of (NH_4)_3 PO_4.12 MoO_3}{Mass of organic compound} \times 100$$

% of
$$P = \frac{62}{222} \times \frac{Mass \ of \ Mg_2 P_2 O_7}{Mass \ of \ organic \ compound} \times 100$$

if a copper spoon is used to stir a solution of aluminium nitrate?

- (a) The solution becomes blue
- (b) There is no reaction
- (c) The spoon will get coated with aluminium
- (d) An alloy of aluminium and copper is formed
- **9.** The oxides which can not act as reductant?
 - (I) CO_{2} (II) SO_3
- (III) P_4O_{10} (IV) NO_2
- (a)(I),(II),(III)
- (b)(II),(III),(IV)
- (c)(I),(II),(IV)
- (d)(III),(IV)
- 10. What is the equivalent weight of $C_{12}H_{22}O_{11}$ in the following reaction?

$$C_{12}H_{22}O_{11} + 36HNO_3 \rightarrow 6H_2C_2O_4 + 36NO_2 + 23H_2O_3$$

- (a) $\frac{342}{36}$ (b) $\frac{342}{12}$ (c) $\frac{342}{22}$ (d) $\frac{342}{3}$

Hydrogen

- 11. The number of hydrogen-bonded water molecule(s) are associated in CuSO₄.5H₂O is
 - (a) 1 (b) 2 (c) 3
- 12. Which of the following is not true?
 - (a) Hardness of water is shown by its behaviour towards soap
 - (b) The temporary hardness is due to the presence of Ca and Mg bicarbonates
 - (c) Permanent hardness is due to the presence of soluble Ca and Mg sulphates and chloride
 - (d) Permanent hardness can be removed by boiling the water
- **13.** The percentage of H_2O_2 in 1.5 N solution is (a) 3.6(b) 2.99(c)2.55(d) 2.4
- 14. Correct order of occlusion property is
 - (a) Pd > Pt > Au > Colloidal Pd > Pt
 - (b) Colloidal Pd > Pd > Pt > Au > Ni
 - (c) Ni < Au > Pt > Pd > Colloidal Pd
 - (d) Au > Pt > Pd > Ni > Colloidal Pd
- 15. 100 mL of tap water containing $Ca(HCO_3)$, was titrated with N/50 HCl with methyl orange as indicator. If 30 mL of HCl were required, the temporary hardness as parts of CaCO₃ per 10⁶ parts of water is
 - (a) 150 ppm
- (b) 300 ppm
- (c) 450 ppm
- (d) 600 ppm

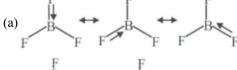
S-Block Elements (Alkali & Alkaline Earth Metals)

- **16.** Which of the alkaline earth metal sulphate is least soluble?
 - (a) BeSO₄
- (b) CaSO₄
- (c) SrSO₄
- (d) $BaSO_{A}$
- 17. Which of the following is used as a source of oxygen in space capsules, submarines and breathing masks?
 - (a) Li,O
- (b) Na₂O₂ (c) KO₂
- (d) K_2O_2
- **18.** A sodium salt of an unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is
- (a) SO_4^{2-} (b) HCO_3^{-} (c) CO_3^{2-}
- (d) NO_{2}^{-}
- 19. BeF, is soluble in water, whereas, the fluorides of other alkaline earth metals are insoluble because of

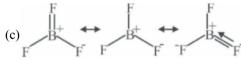
- (a) Ionic nature of BeF,
- (b) Greater hydration energy of Be^{2+} ion
- (c) Covalent nature of BeF,
- (d) None of the above
- **20.** Mixture of *MgCl*, and MgO is called
 - (a) Portland cement
- (b) Sorel's cement
- (c) Double salt
- (d) None

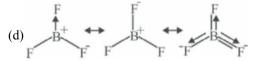
p-Block Elements

- 21. AlCl, is an electron deficient compund but AlF, is not. This is because
 - (a) Atomic size of F is smaller than Cl which makes AlF, more covalent
 - (b) AlCl₃ is a covalent compound while AlF₃ is an ionic compound
 - (c) AlCl₃ exists as a dimer but AlF₃ does not
 - (d) Al in AlCl, is in sp³ hybrid state but Al in AlF, is in sp² state
- 22. Which of the following halides is the most stable?
 - (a) CF_{A}
- (b) *CI*₄
- (c) CBr_4
- (d) CCl_{\perp}
- 23. Different layers in graphite are held together by:
 - (a) Ionic bonding
- (b) Metallic bonding
- (c) Covalent bonding (d) Vanderwaals forces
- 24. Which of the following structures correctly represents the boron trifluoride molecule?









- 25. When SnCl, reacts with HgCl, the product formed are:
 - (a) $Sn + HgCl_A$
- (b) $SnCl_2 + Hg_2Cl_2$



- (c) $SnCl_{\lambda}$ and Hg_{γ}
- (d) None of these

Organic Chemistry (Some Basic Principles & **Techniques**)

- **26.** Homolytic fission of C-C bond in ethane gives an intermediate in which carbon is
 - (a) sp³-hybridised
- (b)sp²-hybridised
- (c)sp-hybridised
- (d) sp²d-hybridised
- 27. In triplet carbenes, the two electrons
 - (a) are paired in one orbital
 - (b) are present in different orbitals
 - (c) have the same spin
 - (d) Both (b) and (c)
- 28. Liquid which decompose below their normal boiling points can be distilled at lower temperature by
 - (a) Increasing the pressure
 - (b) Decreasing the pressure
 - (c) Heating in water bath
 - (d) Heating in sand bath
- 29. Metamers of ethylpropionate are
 - (a) C_4H_0COOH and $HCOOC_4H_0$

- (b) C_4H_9COOH and $CH_3OOC_3H_7$
- (c) CH₃COOCH₃ and CH₃OOC₃H₇
- (d) $CH_3COOC_3H_7$ and $C_3H_7COOCH_3$
- 30. In column chromatography the MOVING PHASE is constituted by
 - (a) A substance which have to be separated
 - (b) Eluent
 - (c) Adsorbent
 - (d) Mixture of eluent and substances to be separated

ANSWER KEY

1. d	2. d	3. d	4. a	5. c
6. c	7. d	8. b	9. a	10. a
11. a	12. d	13. c	14. b	15. b
16. d	17. c	18. b	19. b	20. b
21. b	22. a	23. d	24. a	25. c
26. b	27. d	28. b	29. d	30. d

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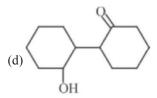
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Questions

ALDEHYDES, KETONES & CARBOXYLICACIDS, CHEMICAL KINETICS

Aldehydes, Ketones & Carboxylic Acids

1. Of the following which is the product formed when cyclohexanone undergoes aldol condensation followed by heating? [2017]



- 2. The product formed by the reaction of an aldehyde with a primary amine is: [2016]
 - (a) Ketone
- (b) Carboxylic acid

- (c) Aromatic acid
- (d) Schiff base
- 3. Reaction of carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is:

[2015]

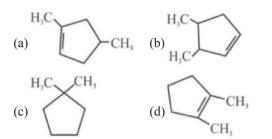
- (a) a Grignard reagent
- (b) hydrazine in presence of feebly acidic solution
- (c) hydrocyanic acid
- (d) sodium hydrogen sulphite
- 4. An organic compound 'X' having molecular formula $C_5H_{10}O$ yield phenylhydrazone and gives negative response to the iodoform test and Tollens'test. It produces n-pentane on reduction. 'X' could be

[2015]

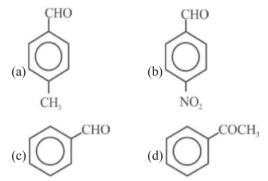
- (a) pentanal
- (b) 2-pentanone
- (c) 3-pentanone
- (d) *n*-amyl alcohol
- 5. Treatment of cyclopentanone with methyllithium gives which of the following species?

[2015]

- (a) Cyclopentanonyl anion
- (b) Cyclopentanonyl cation
- (c) Cyclopentanonyl radical
- (d) Cyclopentanonyl biradical
- 6. A single compound of the structure, [2015] CH₃COCH₂CH(CH₃)CH₂CH₃ is obtainable from ozonolysis of which of the following cyclic compounds?



7. Which one is most reactive towards nucleophilic addition reaction? [2014]



8. Reaction by which Benzaldehyde cannot be [2013] prepared?

9. Consider the following reaction:

is
$$[2012]$$
(a) $C_6H_5COCH_3$ (b) C_6H_5CHO
(c) C_6H_5CI (d) C_6H_5OH

- 10. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is (a) A > C > B > D(b) B > D > C > A(c)A>B>C>D(d) B > A > D > C
- 11. Which of the following compounds will give a yellow precipitate with iodine and alkali? [2012] (a) Acetophenone (b) Methyl acetate
 - (c) Acetamide (d) 2- Hydroxypropane
- 12. Consider the reaction: $RCHO + NH_2NH_2 \rightarrow R - CH = N \ NH_2$ What sort of reaction is it?
 - (a) Electrophilic substitution elimination reaction
 - (b) Nucleophilic addition elimination reaction
 - (c) Electrophilic addition elimination reaction
 - (d) Free radical addition elimination reaction

13. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is [2012]

14. CH_3CHO and $C_6H_5CH_2CHO$ can be

distinguished chemically by

[2012]

- (a) Benedict's test
- (b) Iodoform test
- (c) Tollen's reagent test
- (d) Fehling's solution test
- **15.** Predict the products in the given reaction. [2012]

$$(b) \begin{array}{c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\$$

16. In a set of reaction m-bromobenzoic acid gave a product D. Identify the product D [2011]

COOH
$$A \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow{NaOH Br_2} D$$

$$A \xrightarrow{SOCl_2} COOH$$

- 17. Clemmensen reduction of a ketone is carried out in the presence of which of the following? [2011]
 - (a) Zn-Hg with HCl
- (b) LiAlH₄
- (c) H_2 and Pt as catalyst (d) Glycol with KOH
- **18.** Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine? [2010]
 - (a) Hot. conc. H_2SO_4
- (b) $NaOH + Br_2$
- (c) PCl₅
- (d) Sodalime
- 19. The relative reactivities of acyl compounds towards nucleophilic substitution are in the order

of: [2010

- (a) acyl chloride > ester > acid anhydride > amide
- (b) acyl chloride > acid anhydride > ester > amide
- (c) ester > acyl chloride > amide > acid anhydride
- (d) acid anhydride > amide > ester > acyl chloride
- **20.** Propionic acid with $Br_2 | P$ yields a dibromo product. Its structure would be [2009]

- (d) CH,Br CHBr COOH
- **21.** Trichloroacetaldehyde, *CCl₃CHO* reacts with chlorobenzene in presence of sulphuric acid and produces [2009]

$$(a) CI \longrightarrow CI$$

$$CI$$

$$CI$$

$$(p) CI \longrightarrow CI$$

$$(c)$$
CI \longrightarrow CH \longrightarrow CI

$$(d) \bigcirc \begin{array}{c} CH - CH_2C \\ CH_3 \\ O \\ \end{array}$$

- 23. The correct decreasing order of their reactivity towards hydrolysis is [2007]
 - (i) C₆H₅COCl

(ii)
$$O_2N$$
—COCI
(iii) H_3C COCI
(iv) OHC—COCI

- (a) (iv) > (ii) > (iii) (c)(i) > (ii) > (iii) > (iv)
- (b) (ii) > (iv) > (iii) > (i) (d)(ii) > (iv) > (i) > (iii)
- 24. Which of the following orders is wrong with respect to property indicated? [2007]
 - (a) Benzoic acid > Phenol > Cyclohexanol(Acid
 - (b) Aniline > Cyclohexylamine > Benzamide (Base strength)
 - (c) Formic acid > Acetic acid > Propionic acid (Acid strength)
 - (d) Fluoro acetic acid > Chloro acetic acid > Bromo acetic acid (Acid strength)
- 25. The product formed in aldol condensation is

[2007]

(a) an α,β -unsaturated ester

- (b) a β -hydroxy aldehyde or a β -hydroxy ketone
- (c) an β -hydroxy acid
- (d) an α -hydroxy aldehyde or ketone
- 26. Which of the following on treatment with 50% aqueous NaOH gives alcohols and acid? [2007]
 - (a) CH_3COCH_3
- (b) $C_6H_5CH_7CHO$
- (c) C_6H_5CHO
- (d) CH₃CH₂CH₂CHO
- 27. Reduction of aldehydes and ketones into hydrocarbons using Zn - Hg + HCl conc. is called [2007]
 - (a) Wolff-Kishner reduction
 - (b) Clemmensen reduction
 - (c) Cope reaction
 - (d) Dow reaction

Chemical Kinetics

1. Mechanism of a hypothetical reaction

$$X_2 + Y_2 \rightarrow 2XY$$
 is given below: [2017]

- (i) $X_2 \rightleftharpoons X + X(fast)$
- (ii) $X + Y_2 \rightarrow XY + Y(slow)$
- (iii) $X + Y \rightarrow XY$ (fast)

The overall order of the reaction will be:

- (a) 2
- (b) 0
- (c) 1.5
- 2. A first order reaction has a specific reaction rate of 10^{-2} sec^{-1} . How much time it takes for 20 g of the reactant to reduce to 5g? [2017]
 - (a) 138.6 sec
- (b) 346.5 sec
- (c) 693.0 sec
- (d) 238.6 sec
- 3. The rate of a first-order reaction is 0.04 molL⁻¹S⁻¹ at 10 seconds and 0.03 molL⁻¹S⁻¹ at 20 seconds after initiation of the reaction. The half-life period of the reaction is: [2016]
 - (a) 34.1 s (b) 44.1 s(c) 54.1 s (d) 24.1 s
- 4. The addition of a catalyst during a chemical reaction alters which of the following quantities? [2016] (a) Internal energy (b) Enthalpy
- (c) Activation energy
- (d) Entropy
- 5. The rate constant of the reaction $A \rightarrow B$ is 0.6×10^{-3} mole per second. If the concentration of A is 5 M, then concentration of B after 20 minutes [2015]
- (a) $0.36 \,\mathrm{M}$
- (b) 1.08 M
- (c) 0.72 M
- (d) 3.60 M
- 6. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The

order of the reaction is

- (a) Zero
- (b) First
- (c) Second
- (d) More than zero but less than first
- 7. The activation energy of a reaction can be determined from the slope of which of the following graphs? [2015]
 - (a) $\ln k \text{ vs.} T$
- (b) $\frac{\ln k}{T} vs.T$
- (c) $\ln k \text{ vs.} \frac{1}{\pi}$
- (d) $\frac{T}{\ln k} vs. \frac{1}{T}$
- 8. A reaction having equal energies of activation for forward and reverse reaction has [2013]
 - (a) $\Delta H = \Delta G = \Delta S = 0$ (b) $\Delta S = 0$
 - (c) $\Lambda G = 0$
- (d) $\Delta H = 0$
- **9.** What is the activation energy for a reaction if its rate doubles when the temperature is raised from

 $20^{\circ}C$ to $35^{\circ}C$? $(R = 8.314 J \text{ mol}^{-1}K^{-1})$ [2013]

- (a) $15.1kJ \ mol^{-1}$
- (b) $342kJ \ mol^{-1}$
- (c) $269kJ \ mol^{-1}$
- (d) $34.7kJ \ mol^{-1}$
- **10.** Activation energy (E_a) and rate constants $(k_1 \text{ and } k_2)$ of a chemical reaction at two different temperatures $(T_1 \text{ and } T_2)$ are related by
 - (a) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_1} \frac{1}{T_2} \right)$
 - (b) $\ln \frac{k_2}{k} = -\frac{E_a}{R} \left(\frac{1}{T_c} \frac{1}{T_c} \right)$
 - (c) $\ln \frac{k_2}{k} = -\frac{E_a}{R} \left(\frac{1}{T_c} \frac{1}{T_c} \right)$
 - (d) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} \frac{1}{T_2} \right)$
- 11. In a reaction, $A+B \rightarrow Product$, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled, rate | law for the reaction can be written as [2012]

 - (a) $Rate = k[A][B]^2$ (b) $Rate = k[A]^2[B]^2$

(c) $Rate = k[A]^2[B]$

[2015] I

- (d) Rate = k[A][B]
- 12. In a zero-order reaction for every $10^{\circ} C$ rise of temperature, the rate is doubled. If the temperature is increased from $10^{\circ} C$ to $100^{\circ} C$, the rate of the reaction will become [2012]
 - (a) 265 times
- (b) 128 times
- (c) 64 times
- (d) 512 times
- 13. The rate of the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ can be written in three ways: [2011]

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\frac{d[NO_2]}{d[O_2^t]} = k'[N_2O_5]$$

$$\frac{d[O_2^t]}{dt} = k''[N_2O_5]$$

The relationship between k and k' and k'' are:

- (a) k' = 2k; k'' = 2k
- (b) k' = k; k'' = k
- (c) k' = 2k: k'' = k
- (d) k' = 2k: k'' = k/2
- 14. Which one of the following statements for the order of a reaction is incorrect? [2011]
 - (a) Order is not influenced by stoichiometric coefficient of the reactants.
 - (b) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction.
 - (c) Order of reaction is always whole number.
 - (d) Order can be determined only experimentally.
- 15. During the kinetic study of the reaction

 $2A + B \rightarrow C + D$ following results were obtained.

Initial rate of forma Run[A]in M [B]in Mtion of D in ms⁻¹ 0.10.1 6.0×10^{-3} 0.3 0.2 7.2×10^{-2} III0.3 0.4

 2.88×10^{-1}

IV0.4 0.1 2.40×10^{-2}

On the basis of above data which one is correct? [2010]

- (a) $r = k[A]^2[B]^2$ (b) $r = k[A][B]^2$
- (c) $r = k[A]^2[B]$ (d) r = k[A][B]
- **16.** For the reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$, the rate of

disappearance of N_2O_5 is 6.25×10^{-3} mol $L^{-1}s^{-1}$.

The rate of formation of NO_2 and O_2 will be respectively.

- (a) $6.25 \times 10^{-3} \, mol L^{-1} s^{-1}$ and $3.125 \times 10^{-3} \, mol L^{-1} s^{-1}$
- (b) $1.25 \times 10^{-3} \, mol L^{-1} s^{-1}$ and $3.125 \times 10^{-3} \, mol L^{-1} s^{-1}$
- (c) $6.25 \times 10^{-3} \, mol L^{-1} s^{-1}$ and $6.25 \times 10^{-3} \, mol L^{-1} s^{-1}$
- (d) $1.25 \times 10^{-2} mol L^{-1} s^{-1}$ and $3.125 \times 10^{-3} mol L^{-1} s^{-1}$
- 17. The rate of reaction:

 $2NO + Cl_2 \rightarrow 2NOCl$ is given by the rate, equation rate = $k[NO]^2[Cl_2]$. The value of the rate constant can be increased by [2010]

- (a) Increasing the concentration of the Cl₂
- (b) Increasing the concentration of NO
- (c) Increasing the temperature
- (d) Doing all of these
- **18.** For an endothermic reaction energy of activation is E_a and enthalpy of reaction is ΔH (both in $kJ \ mol^{-1}$). Minimum value of E_a will be [2010]
 - (a) $> \Delta H$ (b) = 0
- (c) $< \Delta H$
- 19. Half-life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction
 - (a) $0.5 \times 10^{-2} \,\mathrm{s}^{-1}$
- (b) $0.5 \times 10^{-3} \, \text{s}^{-1}$
- (c) $5.0 \times 10^{-2} \,\mathrm{s}^{-1}$
- (d) $5.0 \times 10^{-3} \,\mathrm{s}^{-1}$
- **20.** For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$,

if
$$\frac{d[NH_3]}{dt} = 2 \times 10^{-4} \, mol \, L^{-1} s^{-1}$$
, the value of

 $\frac{-d[H_2]}{dt}$ would be: [2009]

- (a) $4 \times 10^{-4} \, mol \, L^{-1} s^{-1}$
- (b) $6 \times 10^{-4} mol L^{-1} s^{-1}$
- (c) $1 \times 10^{-4} \, mol \, L^{-1} s^{-1}$ (d) $3 \times 10^{-4} \, mol \, L^{-1} s^{-1}$
- 21. For the reaction $A + B \rightarrow \text{products}$, it is observed
 - (1) On doubling the initial concentration of A only, the rate of reaction is also doubled and
 - (2) On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate law of this reaction is given by

- (a) $rate = [A][B]^2$
- (b) $rate = k[A]^2[B]^2$

- (c) rate = k[A][B]
- (d) $rate = k[A]^2[B]$
- 22. In the reaction

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$$

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following:

(a)
$$\frac{d[Br_2]}{dt} = \frac{3}{5} \frac{d[Br^-]}{dt}$$
 (b) $\frac{d[Br_2]}{dt} = -\frac{3}{5} \frac{d[Br^-]}{dt}$

(c)
$$\frac{d[Br_2]}{dt} = -\frac{5}{3} \frac{d[Br^-]}{dt}$$
 (d) $\frac{d[Br_2]}{dt} = \frac{5}{3} \frac{d[Br^-]}{dt}$

23. The bromination of acetone that occurs in acid solution is represented by this equation.

$$CH_3COCH_3(aq) + Br_2(aq) \rightarrow$$

$$CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$$

These kinetic data were obtained for given reaction concentrations.

Initial concentrations, M

$[CH_3COCH_3]$	Br_2	$H^{\scriptscriptstyle +}$	Initial rate,
			disappearance of Br ₂
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

Based on these data, the rate equation is

- (a) $rate = k[CH_3COCH_3][Br_3][H^+]$
- (b) $rate = k[CH_3COCH_3][H^+]$
- (c) $rate = k[CH_3COCH_3][Br_3][H^+]^2$
- (d) $rate = k[CH_3COCH_3][Br_2]$
- **24.** The rate constants k_1 and k_2 for two different reactions are $10^{16}e^{-2000/T}$ and $10^{15}e^{-1000/T}$ respectively. The temperature at which $k_1 = k_2$ is

(a) $\frac{1000}{2303}K$

(b) 1000 K

(c) $\frac{2000}{2.303}K$

(d) 2000 K

- 25. If 60% of a first-order reaction was completed in 60 min, 50% of the same reaction would be completed in approximately [2007]
 - (a) 40 min
- (b) 50 min
- (c) 45 min
- (d) 60 min
- **26.** In a first-order reaction $A \rightarrow B$, if K is the rate constant and initial concentration of the reactant is 0.5 M, then half-life is [2007]
 - (a) $\frac{\log_{10} 2}{k}$
- (b) $\frac{0.693}{0.5k}$
- (c) $\frac{\ln 2}{k}$
- (d) $\frac{\ln 2}{k\sqrt{0.5}}$

ANSWER KEY

Aldehydes, Ketones & Carboxylic Acids

1. a	2. d	3. b	4. c	5. a
6. a	7. b	8. a	9. b	10. d
11. a, d	12. b	13. d	14. b	15. c
16. b	17. a	18. b	19. b	20. c
21. c	22. a	23. d	24. b	25. b
26. c	27. b			

Chemical Kinetics

1. c	2. a	3. d	4. c	5. c
6. b	7. c	8. d	9. d	10. b,d
11. c	12. d	13. d	14. c	15. b
16. d	17. c	18. d	19. b	20. d
21. a	22. b	23. b	24. a	25. c
26. c				

HINTS & SOLUTIONS

Aldehydes, Ketones & Carboxylic Acids 1.Sol:

2.Sol:
$$R \subset C = O + H_2 N - R' \xrightarrow{H^+} R \subset R' = \ddot{N} - R'$$
Aldehyde Primary amine $R \subset R'$ Schiffs Base

3.Sol: Reaction of carbonyl compounds with ammonia derivatives is an example of Nucleophilic addition elimination reaction.

phenyl hydrazone Negative iodoform test

$$\Rightarrow$$
 CH₃ $\stackrel{\text{O}}{=}$ C $\stackrel{\text{group is absent}}{=}$

Negative Tollen's test \Rightarrow ketone hence, the compound is 3-pentanone.

CH₃CH₂-C -CH₂CH₃
$$\xrightarrow{\text{Reduction}}$$
 CH₃CH₂CH₂CH₂CH₂CH₃

3-Pentanone n -Pentane $(C_5H_{10}O)$

6..Sol:
$$H_3C$$

$$CH_3 (i) O_3$$

$$CH_3 CH_3$$

$$CH_3 CH_3$$

$$CH_4 CH_5$$

$$CH_5 CH_5$$

$$CH_5 CH_5$$

$$CH_7 CH_7$$

$$CH_7 CH_7$$

7.Sol: Any substituent in the carbonyl compound that increases the positive charge on the carbonyl carbon will increase reactivity towards nucleophilic addition. $-NO_2$, shows -M effect hence

8.Sol: Zn/Hg and HCl reduce carbonyl group to methylene group (Clemmensen reduction).

9.Sol:
$$(COCl \xrightarrow{H_2} C-H)$$

It is Rosenmund's reaction (reduction)

 $CI \leftarrow C - C - OH$ 10.Sol:

$$\begin{array}{c|cccc}
H & O & O \\
\uparrow & \parallel & & \parallel \\
C & C & OH & H & C & OH \\
H & (C) & (D)
\end{array}$$

The presence of electron withdrawing group. in carboxylic acid increases acidic character. Also electron withdrawing nature of F is more than Cl.

iodoform test

It is iodoform reaction. Acetophenone and 2-Hydroxy propane both give a yellow precipitate of CHI₃ (Iodoform) with iodine and alkali.

$$\begin{array}{c}
O \\
C \\
C
\end{array}$$

$$\begin{array}{c}
O \\
C
\end{array}$$

$$\begin{array}{c}
O \\
C
\end{array}$$

$$\begin{array}{c}
O \\
C
\end{array}$$
ONa

Acetophenone

$$CH_3$$
 C
 CH_3
 C
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 C
 CH_3
 C
 CH_3
 C
 CH_3
 C
 C
 CH_3

2-Hydroxy propane

$$\xrightarrow{I_2/NaOH}$$
 CH₃COONa+CHI₃

12.Sol: Consider the reaction:

 $RCHO + NH_2NH_2 \rightarrow RCH = N - NH_2$

The reaction is nucleophilic addition elimination reaction.

$$\begin{array}{c|c} H & H & H \\ \hline I & I & I \\ R-C^{\delta+} + : N-NH_2 & \\ \hline I & I & I \\ O & H & \\ \end{array} \\ \begin{array}{c} R-C & N^{\oplus} - NH_2 \\ \hline I & I \\ O & H & \\ \end{array}$$

$$\begin{array}{c} H \\ \downarrow \\ R - C \\ \downarrow \\ \vdots \\ O \end{array} \xrightarrow{H} NH_2 \xrightarrow{-H_2O} R - CH - N - NH_2$$

13.Sol:

$$CH_{3} - C - CH_{3} + C_{2}H_{5}OH \xrightarrow{HCI} CH_{3} - C - CH_{3}$$

$$CH_{3} - C - CH_{3} + C_{2}H_{5}OH \xrightarrow{HCI} CH_{3} - C - CH_{3}$$

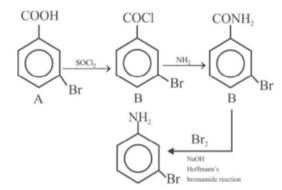
$$OC_{2}H_{5}$$

14. Sol: CH₃CHO will give positive iodoform test as it has CH_3CO –

15.Sol: It is Cannizzaro's reaction.

$$\begin{array}{c|c} CHO & COO \\ \hline \\ Cl & \\ \hline \\ Cl & \\ \end{array} \\ + \begin{array}{c|c} CH_2OH \\ \hline \\ Cl & \\ \end{array}$$

16.Sol:



- **17.Sol:** Clemmensen reduction involves Zn-Hg with HCl to convert > C = O group to $> CH_2$.
- **18.Sol:** This is Hoffmann's bromamide reaction with stepping down of series.
- **19.Sol:** Better is leaving group higher will be reactivity of acyl compound towards nucleophilic acyl substitution. Weaker is its acid and vice-versa.
- **20.Sol:** $CH_3CH_2COOH \rightarrow CH_3CHBr.COOH$

$$\xrightarrow{Br_2/P} CH_3 \xrightarrow{\Gamma} C \xrightarrow{C} COOH$$
Br

This is Hell-Volhard-Zelinsky reaction.

- **21.Sol:** It is preparation of DDT.
- **22.Sol:** It is condensation reaction.

- 23.Sol: The ease of hydrolysis depends upon the magnitude of the +ve charge on the carbonyl group.
- **24.Sol:** Cyclohexylamines are more basic than aniline; the later shows resonance.
- 25.Sol: $CH_3CH_2CHO + CH_3CHO \rightarrow$

$$\begin{matrix} \text{OH} \\ \text{I} \\ \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 \text{CHO} \end{matrix}$$

or

$$CH_3 - CO - CH_3 + CO \longrightarrow CH_3 CH_3 - CH - COCH_3$$

- **26.Sol:** It is Cannizzaro's reaction shown by aldehydes lacking with α -H atom.
- **27. Sol:** It is called Clemmensen reduction.

Chemical Kinetics

1.Sol: According to law of mass action

$$r = k[X][Y,]$$
(i)

from fast step - 1

$$K_{eq} = \frac{[X]^2}{[X_2]}$$

$$[X]^2 = K_{eq}.[X_2]$$

$$[X] = \sqrt{K_{eq}} [X_2]^{1/2}$$
 ...(ii)

From equation (i) & (ii)

$$r = k.\sqrt{K_{eq}}[X_2]^{\frac{1}{2}}[Y_2]$$

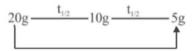
$$r = k'[X_2]^{1/2}[Y_2].$$

Overall order of reaction = 1 + 0.5 = 1.5

2.Sol: Half life of first order reaction $t_{1/2} = \frac{0.693}{k}$

$$=\frac{0.693}{10^{-2}}=69.3 \text{ sec}$$

Method - 1



Total time = $2t_{1/2} = 2 \times 69.3 = 138.6 \text{ sec}$ Method - 2

$$t = \frac{2.303}{\text{k}} \log \frac{[A]_o}{[A]_t}$$

$$t = \frac{2.303}{10^{-2}} \log \frac{20}{5} \Rightarrow t = 138.6 \text{ sec}$$
3.Sol:
$$k = \frac{2.303}{(t_2 - t_1)} \log \frac{(a - x_1)}{(a - x_2)}$$

$$= \frac{2.303}{(20 - 10)} \log \left(\frac{0.04}{0.03}\right)$$

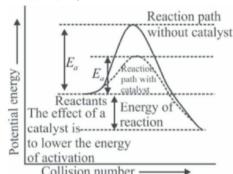
$$= \frac{2.303 \times 0.1249}{10}$$

$$\frac{2.303 \times \log 2}{t_{1/2}} = \frac{2.303 \times 0.1249}{10}$$

$$t_{1/2} = \frac{0.3010 \times 10}{0.1249} = 24.1 \text{ sec}$$

4.Sol: Catalyst can affect only activation energy of the chemical reaction and cannot alter any thermodynamic parameters:

 $(i.e.\Delta H, \Delta G, \Delta S)$



5.Sol: For zero order reaction:

$$x = kt = 0.6 \times 10^{-3} \times 20 \times 60$$

 $x = 0.72M$

6.Sol: Half-life period of a first-order reaction is independent of initial concentration,

$$t_{1/2} = \frac{0.693}{k}$$

7.Sol: Accroding to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

Hence, if ln k is plotted against 1/T, slope of the line will be $-E_a / RT$

8.Sol:
$$\Delta H = (E_a)_f - (E_a)_b = 0$$
9.Sol:
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{293} - \frac{1}{308} \right]$$

$$0.3 = \frac{E_a}{2.303 \times 8.314} \times \frac{15}{293 \times 308}$$

$$E_a = \frac{0.3 \times 2.303 \times 8.314 \times 293 \times 308}{15}$$

$$= 34673 \text{ J mol}^{-1} = 34.7 \text{ J mol}^{-1}$$

10.Sol: On integrating within limits k_1 to k_2 and k_3 and k_4 to T_2

$$\int_{k_{1}}^{k_{2}} \ln k = -\frac{E_{a}}{R} \int_{T_{1}}^{T_{2}} \frac{1}{T}$$

$$\ln \frac{k_{2}}{k_{1}} = \frac{E_{a}}{R} \left[\frac{1}{T_{2}} - \frac{1}{T_{1}} \right] = \frac{E_{a}}{R} \left[\frac{1}{T_{1}} - \frac{1}{T_{2}} \right]$$
or
$$\ln \frac{k_{2}}{k_{1}} = \frac{E_{a}}{R} \left[\frac{1}{T_{1}} - \frac{1}{T_{2}} \right]$$

Options (b) and (d) both are one and the same and are correct.

11.Sol: Let
$$r = k[A]^m[B]^n$$

 $r_1 = k[A]^m[2B]^n$
 $r_2 = k[2A]^m[2B]^n$
Also, $\frac{r_1}{r} = 2$ and $\frac{r_2}{r} = 8$ (Given)

Therefore m = 2 and n = 1

$$\therefore r = k[A]^2[B]^1$$

12.Sol: Rate or rate constant doubles for every 10° or 10K rise in temperature

$$\therefore \frac{r_{100}}{r_{10}} = (2)^9 = 512$$

13.Sol: Rate of disappearance of reactants = Rate of appearance of products

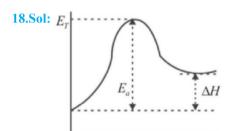
$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{k}{2} = \frac{k'}{4} = k''$$
 $k = 2k, k'' = \frac{k}{2}$

- 14.Sol: Order of reaction may be fractional.
- **15.Sol:** $r = K[A]^m [B]^n$

16.Sol:
$$-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_5]}{dt} = \frac{2d[O_2]}{dt} = R.O.R$$

17.Sol: 15k increases with increase in temperature



19.Sol: For first order:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{13.86} = 5 \times 10^{-4} \,\text{s}^{-1}$$

20.Sol:
$$\frac{1}{2} \frac{d[NH_3]}{dt} = \frac{1}{3} \frac{d[H_2]}{dt}$$

$$\therefore -\frac{d[H_2]}{dt} = \frac{3}{2} \times \frac{d[NH_3]}{dt}$$

$$= \frac{3}{2} \times 2 \times 10^{-4} = 3 \times 10^{-4}$$

21.Sol:
$$r = k[A]^m[B]^n$$
 ...(i)

$$2r=k[2A]^m[B]^n \qquad ...(ii)$$

$$8r = k[2A]^m[2B]^n$$
 ...(iii)

- By (i) and (ii), m = 1
- By (ii) and (iii), n = 2

$$\therefore r = k[A]^1[B]^2$$

22.Sol:
$$\frac{1}{3} \frac{d[Br_2]}{dt} = -\frac{1}{5} \frac{d[Br^-]}{dt} = R.O.R$$

23.Sol: $r = k[CH_3COCH_3]^a [Br_2]^b [H^+]^c$

$$5.7 \times 10^{-5} = k[0.30]^a [0.05]^b [0.05]^c$$
 ...(1)

$$5.7 \times 10^{-5} = k[0.30]^a [0.10]^b [0.05]^c$$
 ...(2)

$$1.2 \times 10^{-4} = k[0.30]^a [0.10]^b [0.10]^c$$
 ...(3)

$$3.1 \times 10^{-4} = k[0.40]^a [0.05]^b [0.20]^c$$
 ...(4)

- By (1) and (2) b = 0
- By (2) and (3) c = 1
- By (3) and (4) a = 1

24.Sol:
$$k_1 = 10^{16} e^{-2000/T}$$
; $k_2 = 10^{15} e^{-1000/T}$

if
$$k_1 = k_2$$
 then $10^{16} e^{-2000/T} = 10^{15} e^{-1000/T}$

or
$$\log 10 - \frac{2000}{T} = -\frac{1000}{T}$$
 or $T = \frac{1000}{2.303} K$

25.Sol:
$$60 = \frac{2.303}{k} \log \frac{100}{40}$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{100}{50}$$

$$\therefore \frac{60}{t} = \frac{0.40}{0.310}$$

$$t = 45 \text{ minute}$$

26.Sol: For *Ist* order reaction,

$$k = \frac{2.303 \log_{10} 2}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{\ln 2}{k}$$

MOCK TEST PAPER

JEE MAIN - 4

2018

CHEMISTRY

- 1. A, B and C are hydroxy-compounds of the elements X, Y and Z respectively. X, Y and Z are in the same period of the periodic table. A gives an aqueous solution of pH less than seven. B reacts with both strong acids and strong alkalies. C gives an aqueous solution which is strongly alkaline Which of the following statements is/are true:
 - I: The three elements are metals
 - II: The electronegativities decrease from X to Y to
 - III: The atomic radius decreases in the order X, Y and Z
 - IV: X, Y and Z could be phosphorus, aluminium and sodium respectively:
 - (a) I, II, III only correct
 - (b) I, III only correct
 - (c) II, IV only correct
 - (d) II, III, IV only correct
- 2. Basic, acidic and amphoteric oxides among them (a) A, B, C (b) B, A, C
 - (c)A,C,B
- (d) B, C, A
- 3. Molecular shapes of SCl_4 , CCl_4 and XeF_4 are
 - (a) Same with 2,0 and 1 lone pairs of electrons respectively
 - (b) Same with 1,1 and 1 lone pairs of electrons respectively
 - (c) Different with 1,0 and 2 lone pairs of electrons respectively
 - (d) Different with 1,1 and 1 lone pairs of electrons respectively
- **4.** KF combines with HF to form KHF_2 . The compound contains the species

- (a) K^+, F^- and H^+ (b) K^+, F^- and HF
- (c) K^+ and $[HF_2]^-$ (d) $[KHF]^+$ and F_2
- 5. $1.75 \,\mathrm{Lof}$ a gas at $127^{\circ}C$ and 5 atm is converted to 2.875 L at 85°C and 1 atm. The percentage of gas escaped is
 - (a) 11.11% (b) 23.2%
- (c) 56.3%
- (d) 63.5%
- 6. A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen. (a) 0.2(b) 0.4(c)0.6(d) 0.8
- 7. At 25°C and 1 atm, N_2O_4 dissociates by the reaction,

$$N_2O_4(g) \Longrightarrow 2NO_2(g)$$

If it is 35% dissociated at given condition, find the volume of above mixture that will diffuse if 20 mL of pure O_2 diffuses in 10 min at same temperature and pressure.

- (a) 13.7 mL (b) 13.7 L (c) 68 mL
- **8.** For a first order reaction $A \rightarrow B$ the reaction rate at which reactant concentration of 0.01 M is found to be 2.0×10^{-5} M sec⁻¹. The half-life period of the reaction is:
 - (a) $30 \, s$ (b) 300 s(c) $220 \, s$ (d) 347s.
- 9. Which of the following statements regarding the molecularity of reaction is wrong?
 - (a) It is the number of molecules of the reactions taking part in a single step chemical reaction.
 - (b) It is calculated from the reaction mechanism.

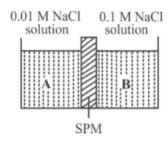
- (c) It may be either a whole number or fractional.
- (d) It depends on the rate determining step in the reaction.
- 10. The specific heat of a gas at constant volume is 0.075 cal/g-K. Predict the atomicity of the gas.

(Molar mass of gas is $40 \ g \ mol^{-1}$.)

(a) 1

(c) 3

- (d) None of these
- 11. Two solutions marked as A and B are separated through semipermeable membrane as below. The phenomenon undergoing



- (a) Na^+ moves from solution A to solution B
- (b) Both Na^+ and Cl^- moves from solution (A) to solution (B)
- (c) Both Na^+ and Cl^- moves from solution (B) to
- (d) Solvent molecules moves from solution (A) to
- 12. A solution is obtained by mixing 300g of 25% solution and 400g of 40% solution by mass. The mass percentage of the resulting solution is:
 - (a) 66.66%
- (b) 3.36%
- (c) 33.6%
- (d) 22.4%
- 13. Molar conductance of 0.1 M acetic acid is

 $7 ohm^{-1} cm^{2}mol^{-1}$. If the molar conductance of acetic acid at infinite dilution $380.8 \ ohm^{-1}cm^2mol^{-1}$, the value of dissociation constant will be:

- (a) $3.38 \times 10^{-5} \, mol \, dm^{-3}$ (b) $226 \times 10^{-5} \, mol \, dm^{-3}$
- (c) $1.66 \times 10^{-3} \, mol \, dm^{-1}$ (d) $1.66 \times 10^{-2} \, mol \, dm^{-3}$
- **14.** Which of the following is crotonic acid?
 - (a) $CH_2 = CH COOH$
 - (b) $C_6H_5 CH = CH COOH$
 - (c) $CH_3 CH = CH COOH$

15. Geometrical isomerism shows

$$(a) \qquad \qquad (b) \qquad \qquad CH_2 \\ (c) \qquad \qquad (d) \qquad \qquad CHCI$$

- 16. Which of the following possesses highest melting point?
 - (a) Chlorobenzene
- (b) o-Dichlorobenzene
- (c) m-Dichlorobenzene
- (d) p-Dichlorobenzene
- 17. The compound "A" when treated with ceric ammonium nitrate solution gives yellow ppt. The compound "A" is
 - (a) Alcohol
- (b) Alkane
- (c) Aldehyde
- (d) Acid
- **18.** $C_6H_5COCOC_6H_5 \xrightarrow{OH^-} (C_6H_5)_2C(OH)COOH$.

The above reaction is known as

- (a) Beckmann rearrangement
- (b) Benzilic acid rearrangement
- (c) Benzoin condensation
- (d) Aldol condensation
- 19. The pair of amphoteric hydroxides is
 - (a) $Al(OH)_3$, LiOH
- (b) $Be(OH)_{2}$, $Mg(OH)_{2}$
- (c) $B(OH)_3$, $Be(OH)_3$
- (d) $Be(OH)_{2}$, $Zn(OH)_{2}$
- 20. Lithopone is a mixture of:
 - (a) Barium sulphate and zinc sulphide
 - (b) Barium sulphide and zinc sulphide
 - (c) Calcium sulphate and zinc sulphide
 - (d) Calcium sulphide and zinc sulphide
- 21. Acidified potassium dichromate oxidises
 - I. Iodides to iodine
 - II. Sulphides to sulphur
 - III. Tin (IV) to tin (II)
 - IV. Iron (III) salts to iron (II) salts

The appropriate option with correct choices are

- (a) I, II and III
- (b) II, III and IV
- (c) I and IV
- (d) I and II
- 22. Gun metal contains
 - (a) Cu, Sn, Zn
- (b) Cu, Ni
- (c) Cu, Ni, Fe
- (d) Cu, Sn, P
- complex compound $[Cu(NH_3)_4][PtCl_4]$ is

23. The total number of possible isomers of the

- (a) 4
- (b) 3
- (c) 6

- 24. The coagulation values of AlCl₃ and NaCl are 0.093 and 52 respectively. Then coagulating power of AlCl, as compared to that of NaCl is
 - (a) 52×0.093 times
- (b) 52/0.093 times
- (c) 0.093/52 (d) 52-0.093 times
- 25. The number of Nucleotide pairs present in one turn of DNA helix is
 - (a) 10
- (c) 8
- 26. The end product (B) formed in the reaction sequence
 - Glucose $\xrightarrow{\text{HCN}} A \xrightarrow{\text{HI,P}} B$
 - (a) Hexanoic acid
- (b) Hexane
- (c) Heptane
- (d) Heptanoic acid
- 27. In the oxyacids of chlorine Cl O bond contains
 - (a) $p\pi d\pi$ bonding
 - (b) $p\pi p\pi$ bonding
 - (c) $d\pi d\pi$ bonding
 - (d) None of these
- 28. The term "fools gold" is used for a mineral which shines like gold. It is
 - (a) Iron pyrites
- (b) Copper pyrites
- (c) Cinnabar
- (d) Cadmium sulphide
- 29. Which process of reduction of mineral to the metal is suited for the extraction of copper from its ores with low copper content?
 - (a) Metal displacement
 - (b) Auto reduction
 - (c) Chemical reduction
 - (d) Electrolytic reduction
- 30. Which of the following layering pattern will have a void fraction of 0.26?
 - (a) ABCCBABC
- (b) ABBAABBA
- (c) ABCABCABC
- (d) ABCAABCA

ANSWER KEY

1. c 2. c 3. c **4.** c 5. d **6.** d **7.** a **8.** d 9. c **10.** a **11.** d **12.** c **13.** a **14.** c 15. d **16.** d 17. a 18. c **19.** d **20.** a **21.** d **22.** c **23.** d **24.** b **25.** a **27.** a **26.** c **28.** b **29.** b **30.** c

HINTS & SOLUTIONS

- 2.Sol: CaO, SO₃, Al₂O₃
- 3.Sol: In SCl₄,

number of bond pairs = 4

number of lone pairs = 1

In CCl₄,

number of bond pairs = 4

number of lone pairs = 0

In XeF₄,

number of bond pairs = 4

number of lone pairs = 2

4.Sol: F- forms H-bond with HF, therefore, the species

 $[H....F - H]^-$ or HF_2 exists.

5.Sol:
$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{5 \times 1.75}{400} \times \frac{360}{1} = 7.875L$$

Percentage escaped

$$= \frac{7.875 - 2.875}{7.875} \times 100 = 63.5\%$$

6.Sol:
$$n_{H_2} = \frac{20}{2}$$
 $n_{O_2} = \frac{80}{32}$

$$p_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{O_2}} \times P$$
.

7.Sol:
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$\begin{array}{ccc}
1 & 0 \\
1-\alpha & 2\alpha
\end{array}$$

$$\therefore \sum n = 1 + \alpha$$

$$K_P = \frac{4\alpha^2 P}{1 - \alpha^2} = \frac{4(0.35)^2(1)}{1 - (0.35)^2} = 0.56atm$$

$$\frac{1+\alpha}{1} = \frac{\left(MW_{Mixture}\right)_{Initial}}{\left(MW_{Mixture}\right)_{Eincl}} = \frac{\left(MW_{N_2O_4}\right)}{\left(MW_{Mixture}\right)_{Eincl}}$$

$$1 + 0.35 = \frac{92}{\left(MW_{Mixture}\right)_{Final}}$$

$$MW_{Mixture} = 68.15$$

Let, V(mL) be the volume of mixture diffused in. From Graham's law of diffusion,

$$\frac{r_{O_2}}{r_{Mixture}} \sqrt{\frac{MW_{Mixture}}{MW_{O_2}}} \Rightarrow \frac{20/10}{V/10} = \sqrt{\frac{68.15}{32}}$$

$$V = 13.70 mL$$

8.Sol: rate = $k[A]^1$

$$k = \frac{2.0 \times 10^{-5}}{0.01} = 2.0 \times 10^{-3}$$

$$\therefore t_{1/2} = \frac{0.693}{2.0 \times 10^{-3}} = 347 \text{ s}$$

9.Sol: Molecularity can never be fractional.

10.Sol:
$$C_v = 0.075 \times 40 = 3 \ cal \ K^{-1} \ mol^{-1}$$

$$C_p - C_v = R$$

$$\Rightarrow C_p - 3 = 2 \Rightarrow C_p = 5 \ cal \ K^{-1} mol^{-1}$$

$$\gamma = \frac{C_p}{C} = \frac{5}{3} = 1.66$$

Thus, the gas is monoatomic.

12.Sol: Mass percentage of solute in the solution

13.Sol:
$$K_a = C\alpha^2 = 0.1 \times \left(\frac{7}{380.8}\right)^2 = 3.38 \times 10^{-5}$$

16.Sol: Due to symmetrical structure, p-dichlorobenzene fits closely in the crystal lattice.

17.Sol:

$$\begin{array}{ll} R-OH+(NH_4)_2Ce(NO_3)_6 & \longrightarrow Ce(NO_3)_6(ROH)_9+N_2+14NO_3 \\ \text{alcohol} & \text{cerric amine. nitrate} & \text{yellow ppt.} \end{array}$$

20.Sol: Lithopone is used as paint.

21.Sol: Acidified potassium dichromate oxidises iodides to iodine, sulphides to sulphur, tin (II) to tin(IV), iron (II) salts to iron (III).

23.Sol: The possible isomers of the complex are

$$[Cu(NH_3)_3Cl][PtCl_3NH_3],$$

$$[\operatorname{Cu}(\operatorname{NH_3})_2\operatorname{Cl_2}][\operatorname{Pt}(\operatorname{NH_3})_2\operatorname{Cl_2}],$$

$$[Cu(NH_3)Cl_3][Pt(NH_3)_3Cl]$$

$$[CuCl_4][Pt(NH_3)_4]$$

The total number of isomers is five.

Coagulation power of AlCl₃

24.Sol: Coagulation power of NaCl

$$= \frac{\text{Coagulation value of NaCl}}{\text{Coagulation value of AlCl}_3}$$

26.Sol: Compound A is glucose cyanohydrin. Compound B is Heptane.

Compound B is I

27.Sol:
$$Cl \longrightarrow O$$

$$\downarrow \qquad \qquad \downarrow$$

$$d\pi \qquad p\pi$$

Oxygen doesn't have vacant "d" orbitals in the valence shell and only $p\pi$ electron participates and chlorine has vacant "d" orbital in valences shell thus only $d\pi$ electron participates.

28.Sol: Copper pyrites or chalcopyrite (CuFeS₂) is known as fools gold.

29.Sol: Auto reduction is used for the extraction of copper from its ore with low copper content.



Previous year **EEMAN**

Questions

COORDINATION COMPOUNDS

[ONLINE QUESTIONS]

- 1. Identify the correct trend given below: [2016] (Atomic No.: Ti = 22, Cr = 24 and Mo = 42)
 - (a) Δ_{\circ} of $[Cr(H_{2}O)_{6}]^{2+} < [Mo(H_{2}O)_{6}]^{2+}$ and
 - Δ_{0} of $[Ti(H_{2}O)_{6}]^{3+} < [Ti(H_{2}O)_{6}]^{2+}$
 - (b) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_{\circ} of $\left[\text{Ti}(H_{\circ}O)_{\epsilon} \right]^{3+} > \left[\text{Ti}(H_{\circ}O)_{\epsilon} \right]^{2+}$
 - (c) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and
 - Δ_{0} of $[Ti(H_{2}O)_{6}]^{3+} < [Ti(H_{2}O)_{6}]^{2+}$
 - (d) $\Delta_{\circ} of \left[Cr(H_2O)_6 \right]^{2+} < \left[Mo(H_2O)_6 \right]^{2+}$ and Δ_{0} of $[Ti(H_{2}O)_{6}]^{3+} > [Ti(H_{2}O)_{6}]^{2+}$
- 2. Which one of the following complexes will
- consume more equivalents of aqueous solution of [2016] $Ag(NO_3)$?
 - (a) Na₃[CrCl₆]
- (b) [Cr(H,O), Cl]Cl,
- (c) $[Cr(H_2O)_6]Cl_3$
- (d) $Na_{2}[CrCl_{5}(H_{2}O)]$
- 3. Which of the following is an example of homoleptic complex? [2016]
 - (a) $[Co(NH_3)_4Cl_2]$
- (b) $[Co(NH_3)_6]Cl_3$
- (c) [Co(NH₃)₅Cl]Cl₂
- (d) $[Pt(NH_3)_2Cl_2]$

- 4. When concentrated HCl is added to an aqueous solution of CoCl₂, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction? [2015]
 - (a) $[CoCl_6]^{3-}$
- (b) [CoCl₆]⁴⁻
- (c) $[Co(H_2O)_6]^{2+}$
- (d) [CoCl₄]²⁻
- 5. Which of the following complex ions has electrons that are symmetrically filled in both t_{2g} and e_g orbitals? [2015]
 - (a) $[FeF_3]^{3-}$
- (b) $[CoF_6]^{3-}$
- (c) $[Co(NH_3)_6]^{2+}$
- (d) $[Mn(CN)_6]^{4-}$
- **6.** Nickel (Z = 28) combines with a uninegative monodentate ligand to form a diamagnetic complex $[NiL_4]^{2-}$. The hybridisation involved and the number of unpaired electrons present in the complex are respectively: [2014]
 - (a) sp³, zero
- (b) sp³, two
- (c) dsp², one
- (d) dsp², zero
- 7. An octahedral complex with molecular composition M.5NH₃.Cl.SO₄ has two isomers, A and B. The solution of A gives a white precipitate with AgNO₃ solution and the solution of B gives white precipitate with BaCl, solution. The type of isomerism exhibited by the complex is: [2014]

- (a) Geometrical isomerism(b) Coordinate isomerism
- (c) Ionisation isomerism (d) Linkage isomerism
- 8. Which of the following name formula combinations | is not correct? [2014]

Formula

Name

- (a) K[Cr(NH₃)₂Cl₄] Pottassium diamine Tetrachlorochromate III
- (b) [CO(NH₃)₄(H₂O)I]SO₄ Tetraamine aquaiodo cobalt (III) sulphate
- (c) [Mn(CN)₅]²⁻ Pentacynomagnate (II) ion
- (d) K₂[Pt(CN)₄] Potassium tetracyanoplatinate (II)
- Consider the coordination compound,
 [Co(NH₃)₆]Cl₃. In the formation of this complex,
 the species which acts as the Lewis acid is:

[2014]

- (a) NH₃
- (p) CI_
- (c) $[Co(NH_3)]^{3+}$
- (d) Co^{3+}
- 10. The correct statement about the magnetic properties of $[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$ is: (Z=26). [2014]
 - (a) $[Fe(CN)_6]^{3-}$ is paramagnetic, $[FeF_6]^{3-}$ is diamagnetic.
 - (b) Both are diamagnetic
 - (c) $[Fe(CN)_6]^{3-}$ is diamagnetic, $[FeF_6]^{3-}$ is paramagnetic.
 - (d) Both are paramagnetic

ANSWER KEY

1. a 2. c 3. b 4. d 5. a 6. d 7. c 8. c 9. d 10. d

HINTS & SOLUTIONS

1. Sol: $\Delta_0 \propto \text{CFSE}$ (Crystal field stabilisation energy)

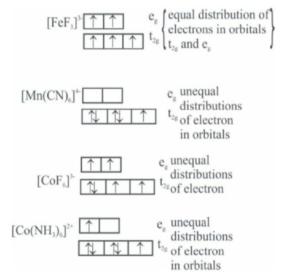
$$\Delta_{\scriptscriptstyle o} of \big[Cr(H_2O)_6 \big]^{2+} < \Delta_{\scriptscriptstyle o} of \big[Mo(H_2O)_6 \big]^{2+}$$

Because here $\Delta_{\rm o}$ depends on $Z_{\rm eff}$ & $Z_{\rm eff}$ of 4d

series is more than 3d series.

But
$$\Delta_{\circ}$$
 of $\left[\mathrm{Ti}(\mathrm{H_2O})_6\right]^{3+} < \Delta_{\circ}$ of $\left[\mathrm{Ti}(\mathrm{H_2O})_6\right]^{2+}$

- Sol: Complex [Cr(H₂O)₆]Cl₃ will consume more equivalents of aqueous solution of Ag(NO₃).
- **3.Sol:** Complex having only 1 type of ligands are examples of homoleptic complex.
- **4.Sol:** Aqueous of solution of CoCl₂
 - contains $[Co(H_2O)_6]^{2+}$ which is pinkish in colour so option d is incorrect.
 - Reduction potential of $Co^{3\oplus} \rightarrow Co^{2\oplus}$ is high so option (b) is incorrect. Co^{2+} does not oxidise easily to Co^{3+} .
 - It a general case that symmetrial substituted octahedral complexes are less deeper in colour than tetrahedral complexes. So [CoCl₄]²⁻ is deep blue in colour.
- **5.Sol:** Symmetrically filled t_{2g} and e_{g} are those which contain equal distribution of electrons.



- **8. Sol:** Correct Name of [Mn(CN)₅]²⁻ is Pentacynomagnate (III) ion.
- Sol: Metalcation i.e., Ca³⁺ acts as a lewis acid which accept lone pair from ligands of NH₃.
- **10.Sol:** In $[FeF_6]^{3-}$, 5 unpaired electron present. In $[Fe(CN)_6]^{3-}$ 1 unpaired electron present.

CHEMIS TRICKS

By: A.N.S. SANKARARAO (Hyderabad)

Some of the competitive exams are either based on only XII class syllabus or based on maximum questions from XII class syllabus. You have enjoyed with XI class shortcuts, memory tips and chemistricks in February 2019 issue, now you will get XII class in this issue.

SOLID STATE

• Contributuion of an atom at body centre =1, face centre = $\frac{1}{2}$, edge = $\frac{1}{4}$, corner = $\frac{1}{8}$

Net No. of constituent particles in

→ Simple unit cell =
$$8 \times \frac{1}{8}$$
 (corners) = 1

⇒ F. C. C. unit cell
$$= 8 \times \frac{1}{8}$$
 (corners) $+6 \times \frac{1}{2}$ (faces)=4
⇒ B. C. C. unit cell $= 8 \times \frac{1}{8}$ (corners) $+1 \times 1$ (Body) = 2

$$\rightarrow$$
 B. C. C. unit cell = $8 \times \frac{1}{8}$ (corners) +1×1 (Body) = 2

→ End centre unit cell=
$$= 8 \times \frac{1}{8}$$
 (corners) $+2 \times \frac{1}{2}$ (faces) = 2

CHEMISTRICK for 7 crystal systems CUTE ORTHE TRY MONDAY. If she slaps TRYCLINIC

Crystal System	Axial Characteristics	Angular Characteristics	No. of Bravais Lattices	No. of Lattices	Examples
CUBIC	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$	3	S, B, F	NaCl, CaF ₂ ZnS, Diamond
TETRAGONAL	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	2	S, B	SnO ₂ , TiO ₂
ORTHO- RHOMBIC	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	4	S, B, F,E	Match Box, KNO ₃ , BaSO ₄ , MgSO ₄ .7H ₂ O
HEXAGONAL	$a = b \neq c$	$\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$	1	S	Graphite, Ice, Quartz, HgS
TRIGONAL	a = b = c	$\alpha = \beta = \gamma \neq 90^{\circ}$	1	S	NaNO ₃ , KMnO ₄ , Bi, As, Sb
MONOCLINIC	$a \neq b \neq c$	$\alpha = \beta \neq \gamma = 90^{\circ}$	2	S, E	FeSO ₄ .7H ₂ O, CaSO ₄ .2H ₂ O
TRICLINIC	$a \neq b \neq \mathbf{c}$	$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$	1	S	CuSO ₄ .5H ₂ O Boric acid, K ₂ Cr ₂ O ₇

S = Simple cubic or primitive,

F = FCC, B = BCC, E = End centred

CHEMISTRICK for No. of Bravias lattices:

Reading 3 to (2) 4 is not enough, Read from 11 to (2) 1.

O Radius ratio = r_{cation} / r_{anion}

Radius ratio	Shape of the crystal	Coordination number
upto 0.1	Linear	2
0.1 to 0.2	Trigonal	3
0.2 to 0.4	Tetrahedral	4
0.4 to 0.7	Square planar	4
0.4 to 0.7	Octahedral	6
> 0.7	Cubic	8

• n atoms = n Octahedral Voids = 2n Tetrahedral voids





O Radius ratio of

Tetrahedral voids =
$$\frac{r_{Void}}{r_{Sphere}}$$
 = 0.225

Octahedral Voids =
$$\frac{r_{Void}}{r_{Sphere}} = 0.414$$

- O Each unit cell of NaCl consists 14Cl ions & 13Na⁺ ions
- O Nearest neighbour distance (d):

Simple cubic : BCC : FCC = $a : \frac{\sqrt{3}}{2}a : \frac{1}{\sqrt{2}} \cdot a$

= 1a : 0.86a : 0.7a

O Radii (r):

Simple cubic : BCC : FCC = $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}} \cdot a$

= 0.5 a : 0.43 a : 0.35 a

O Packing fraction:

Simple cubic : BCC : FCC = 0.52 : 0.68 : 0.74

O Packing efficiency:

Simple cubic : BCC : FCC = 52% : 68% : 74%

O Vacant space:

Simple cubic : BCC : FCC = 48% : 32% : 26%

- O Edge length of **NaCl** (FCC) = $2(r_c + r_a) = a$
- O Edge length of *CsCl* (BCC) = $2(r_a + r_a) = \sqrt{3} \cdot a$
- \bigcirc HCP = AB AB AB.....
- O FCC or CCP = ABC ABC ABC
- O SemiConductors P e n

P-type: dope III (B, Al) with IV (Si, Ge) **n-type:** dope V (P, As) with IV (Si, Ge)(e) e equilibrium group IV i.e. middle of III & V)

O Density $(\rho) = \frac{Z \times M}{a^3 \times N_4}$

(z = no. of atoms in unit cell, a = edge length)

Schottky defect (NaCl, KCl, CsCl, AgBr)

Shortage of ions

Fall into interstice

- Frenkel defect
 (ZnS, AgCl, AgBr, AgI)
- $O n\lambda = 2d \sin \theta \text{ (Bragg's equation)}$
- O F- Centres: gives colour when anionic site is occupied by unpaired e^-
 - \rightarrow NaCl+Na (excess): Yellow
 - → LiCl + Li (excess): Pink
 - \rightarrow KCl+K (excess): Violet

CHEMISTRICK: KV Li P is So(sodium) Yellow. Why?

O Paramagnetic: (B>H)

eg: Cr^{+3} , Fe^{+2} & Fe^{+3} , Cu^{+2} , O_2

- O Diamagnetic: (B < < < < H) eg: H_2O , C_6H_6 , ZnO, KCl, NaCl
- O Ferrimagnetic: $\uparrow \uparrow \downarrow \uparrow \uparrow \downarrow$ eg: $CuFe_2O_4$, $ZnFe_2O_4$ like Ferrites
- O Anti Ferromagnetic: $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$

eg: V_2O_3 , MnO_2

SOLUTIONS

 $O_{ppm} = \frac{No. of parts of one component}{No. of parts of all components} \times 10^{6}$

- \mathbf{O} $N = M \times Basicity(for\ acid)$
- \mathbf{O} $N = M \times Acidity(for base)$
- $M_{mix} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$
- $N_{mix} = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$
- **O** Neutralisation:

$$\frac{M_a V_a}{n_a} = \frac{M_b V_b}{n_b}$$

 $N_a V_a = N_b V_b$

Q Dilution:

$$M_1V_1 = M_2V_2$$

- O Vol. of Water added = $V_2 V_1$
- O No. of Milli moles = $M \times V$
- O No. of moles = $\frac{M \times V}{1000}$
- O No. of Milli equivalents = $N \times V$
- O No. of equivalents = $\frac{N \times V}{1000}$
- O Mole fraction of solvent $(X_1) = \frac{n_1}{n_1 + n_2}$
- O Mole fraction of solute $(X_2) = \frac{n_2}{n_1 + n_2}$
- $\mathbf{O} X_1 + X_2 = 1$
- O For aqueous solutions $X_{Solute} = \frac{n_2}{n_2 + 55.5}$
- $Ombiglity(m) = \frac{1000M}{1000d M \cdot M_{soluto}}$
- $\mathbf{O} \mathbf{P}_{gas} = K_H \cdot X_{gas}$
- $K_{\rm H} \alpha \frac{1}{\text{Solubility}} \alpha T$
- O To prevent bends, scuba divers are filled with mixture contains 11.7% He + 56.2% N₂+ 32.1% O₃
- $Q P_{total} = X_1 P_1^0 + X_2 P_2^0$
- $P^0 P = X_2 = \frac{n_2}{n_1 + n_2}$ (1=solvent, 2= solute)
- O Ideal solution obeys Raoult's law,

$$\Delta V_{\rm mix} = \Delta H_{\rm mix} = 0$$

eg: $C_6H_6 + C_6H_5 - CH_3$, n-Hexane + n-Heptane, $C_2H_5Br + C_2H_5Cl$

• +ve deviation: $\Delta H > 0$, $\Delta V > 0$

eg: $C_2H_5OH + CH_2COCH_2$.

 $C_2H_5OH + H_2O_3CHCl_2 + CCl_4$

 \bigcirc -ve deviation: $\triangle H < 0$. $\triangle V < 0$

eg: $C_6H_5OH + C_6H_5NH_2$, $CHCl_3 + CH_3COCH_3$

Q Azeotropes: $95\% C_2H_5OH + 5\% H_2O$,

 $68\% \ HNO_3 + 32\% \ H_2O$

O No. of solute particles \propto B.P \propto L.V.P \propto T_b

 $\propto T_f \propto \frac{1}{VR} \propto \frac{1}{ER}$

- $\Delta T_{\epsilon} = T_0 T_{\epsilon} = i \cdot K_{\epsilon} \cdot m$
- \bigcirc $\pi V = nTR$ ($\pi = Osmotic pressure$)
- \bigcirc π of 1 lit. soln of 1M = 22.4 atm (at 0°C)
- \bigcirc $\pi_1 = \pi_2$ (**Isotonic** solution)
- O Degree of dissociation $\alpha = \frac{i-1}{n-1}$
- O Degree of association $\alpha = \frac{1-i}{1-\frac{1}{2}}$
- O Hypotonic solution: low π , Haemolysis,

[salt] $< 0.9\% \left(\frac{w}{w}\right)$, Water flow into cell & burst.

O Hypertonic solution: high π , plasmolysis,

[salt] > $0.9\% \left(\frac{w}{w}\right)$, Water flow out of cell & shrink.

ELECTRO CHEMISTRY

- Resistance $R = \rho \frac{l}{l} (units : ohm)$
- O conductance $C = \frac{1}{R} = \frac{1}{2} \cdot \frac{a}{I} (ohm^{-1} \text{ or siemen})$
- O Specific resistance or Resistivity

 $(\rho) = R \cdot \frac{a}{1} (ohm \ m)$

O Specific Conductance or Conductivity

$$(K) = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a} = C \cdot \frac{l}{a} \ (ohm^{-1} \ m^{-1})$$

O Molar Conductivity

$$(\Lambda_m) = \frac{K \times 1000}{M} \ (ohm^{-1} \ m^2 \ mol^{-1})$$

O Equivalent conductivity

$$(\Lambda_{eq}) = \frac{K \times 1000}{N} \ (ohm^{-1} \ m^2 \ equivalent^{-1})$$

- O $\Lambda_c = \Lambda_0 b\sqrt{c}$ (slope = -b, intercept = Λ_0)

- $\Lambda_m^0(BaCl_2) = \lambda_{Ba^{+2}}^0 + 2\lambda_{Cl^{-1}}^0$

 $-\frac{1}{2}\lambda_m^0(BaCl_2)$

O Solubility $(S) = \frac{K_{Salt} \cdot 1000}{\Lambda_m^0}$

- For cation electrode $E_{Cell} = E_{Cell}^0 + \frac{0.059}{n} \log C$
- For Anion electrode $E_{Cell} = E_{Cell}^0 \frac{0.059}{n} \log C$
- O For $Zn + 2Ag^+(aq.) \rightarrow Zn^{+2}(aq.) + 2Ag$

$$E_{Cell} = E_{Cell}^{0} + \frac{0.059}{n} \log \frac{\left[Ag^{+}\right]^{2}}{\left[Zn^{+2}\right]}$$

- $E_{Cell} = -0.059 pH$ (for Hydrogen electrode at $25^{\circ}C$)
- $\Delta G^0 = -2.303RT \log K_C$ $= -nFE_{cell}^0$
- $O E_{Cell}^0 = \frac{0.059}{n} \log K_C$
- Thermodynamic efficiency of fuel cell = $\frac{\Delta G_m^0}{\Delta H_m^0}$
- O Products in electrolysis of aqueous electrolyte: If Cu, Ag, Au, Pt, halogens are present we will get them, if not H₂ at cathode, O₂ at anode will be liberated

eg: aq.K₂SO₄ on electrolysis gives H₂ at cathode, O₂ at anode.

aq.CuSO₄ gives Cu at cathode, O₂ at anode with Pt electrodes.

S.No.	Electrolyte	Cathode	Anode	At Cathode	At Anode
1.	K ₂ SO ₄ (aq)	Pt	Pt	H_2	O_2
2.	MgCl ₂ (fused)	Steel	Graphite	Mg	Cl ₂
3.	NaCl(molten)	Pt	Pt	Na	Cl ₂
4.	NaCl(aq)	Pt	Pt	H_2	Cl ₂
5.	Al ₂ O ₃ (fused) cryolite	Graphite	Graphite	Al	O ₂
6.	50% H ₂ SO ₄ (aq)	Pt	Pt	H_2	$H_2S_2O_8$

S.No.	Electrolyte	Cathode	Anode	At Cathode	At Anode
7.	NiCl ₂ (fused)	Pt	Pt	Ni	Cl_2
8.	CuCl ₂ (molten)	Pt	Pt	Cu	Cl ₂
9.	CuSO ₄ (aq)	Pt	Pt	Cu	O_2
10.	CuSO ₄ (aq)	Pt	Cu	Cu	Cu ₂
11.	AgNO ₃ (aq)	Pt	Pt	Ag	O_2
12.	AgNO ₃ (aq)	Pt	Ag	Ag	Ag^{+}
13.	NaOH(molten)	Pt	Pt	N ₂	O_2
14.	NaOH(aq)	Pt	Pt	H_2	O_2
15.	NaH(molten)	Pt	Pt	Na	H_2
16.	RCOONa(aq)	Pt	Pt	H ₂ , NaOH (left solution)	R-R CO ₂

- O Faraday's 1st law $m = c \cdot e \cdot t$ (TRICK: m = cet pronounce as EAMCET)
- O 1F=96,500C = can deposit 1Equivalent
- O Faraday's 2nd law $\frac{W_1}{W_2} = \frac{E_1}{E_2}$
- O CHEMISTRICK for Electro Chemical Series is
 - "LipoBa Call **Naturally** while MagisterAll Man are Zingy and Crossing Sir (Potassium) (Natrium) (Kailum) (Sodium)

by Ferry (boat). Cadet Coach **Nitin** leads Highly Cupid, Ideal, mercy, (Plumbum) (Stannum) (mercury) (Hydrargyrum)

Silly Broad minded, Class Augumentative Fellows" (Silver) (Argentum)

O $S.R.P.(E^0)$ α oxidising power

$$\alpha \frac{1}{reducing \ power}$$

 $\mathbf{O} \quad E_{\mathit{Cell}} = E_{\mathit{Right}} - E_{\mathit{left}}$ To calculate $E_{\rm cell}$ problems easily follow the table:

S.NO	L.H.S (Anode)	R.H.S(Cathode)
1	high-ve S.R.P.	low -ve S.R.P.
2	low ve S.R.P.	high+ve S.R.P.
3	only -ve S.R.P.	only +ve S.R.P.

• Lead accumulator:

$$Pb + PbO_2 + 2H_2SO_4 \xrightarrow{\text{discharging}} 2PbSO_4 + 2H_2O$$

CHEMICAL KINETICS

For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

O rate =
$$-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

O rate
$$= k[N_2][H_2]^3$$

- $O k = A \cdot e^{-E_a/RT}$
- $\log \frac{k_2}{k_1} = \frac{E_a}{2 \cdot 303R} \left[\frac{1}{T_1} \frac{1}{T_2} \right]$
- For zero order reaction $k = \frac{1}{t} \{ [A]_0 [A] \}$
- For 1st order reaction $k = \frac{2 \cdot 303}{t} \log \frac{a}{a x}$
- O Half life $\left(t_{\frac{1}{2}}\right)$ for zero order reaction = $\frac{[A]_0}{2k}$
- For 1st order reaction $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$O \frac{t'_{\frac{1}{2}}}{t''_{\frac{1}{2}}} = \left(\frac{a''}{a'}\right)^{n-1}$$

- O $t_{50\%}$: $t_{75\%}$: $t_{87.5\%}$: $t_{93.75\%} = 1:2:3:4$
- O $t_{90\%}$: $t_{99\%}$: $t_{99.9\%}$: $t_{99.99\%}$ = 1:2:3:4
- O Specific rate $k = P \cdot z \cdot e^{-E_a/RT}$ (P= probability factor)

$$\Delta H = (E_a)_{forward\ reaction} - (E_a)_{backward\ reaction}$$

SURFACE CHEMISTRY

• Freundlich adsorption isotherm $\frac{x}{m} = K \cdot P^{\frac{1}{n}}$

$$(\frac{1}{n} \text{ can have values 0 to 1})$$

(Slope =
$$\frac{1}{n}$$
, intercept = log K)

- O Langmuir adsorption isotherm $\frac{x}{m} = \frac{aP}{1+bP}$
- O Adsorption αT_C
- **O** For adsorption $\Delta H = -ve$, $\Delta S = -ve$, $\Delta G = -ve$
- O Amount of adsorption:

$$SO_2 > NH_3 > CO_2 > CH_4 > N_2 > H_2$$

- O **Zeolites:** good shape selective catalysts, water softners
- O YEAST: source of Zymase, Invertase, Maltase enzymes

TRICK: ZYM (ZIM) is in the EAST (YEAST)

S.No.	Enzyme	Source	Enzyme used in the reaction
I	Nuclease	Nucleus	DNA and RNA → Nucleotides
II	Insuline	Lever	Glucose → Glycogen
III	Lactic Dehydrogenose	Curd	Milk → Curd
IV	Trypsin	Intestine	Proteins → Amino acid
V	Tylene	Saliva	Starch → Maltose
VI	Lypase	Intestine	Lipid(fat) → Fatty acid and glycerides
VII	Pepsin	Stomach	Proteins → Amino acid
VIII	Urease	Soyabean	Urea → Ammonia and CO ₂
IX	Maltase	Yeast	Maltose → Glucose
X	Diastase	Malt	Starch → Maltose
XI	Zymase	Yeast	Glucose → Ethyl alcohol and carbondioxide
XII	Invertase	Yeast	Sucrose → Glucose and Fructose

Dispersed phase	Dispersion medium	Designation	Examples	
Gas	Gas	-	Unknown	
Gas	Liquid	Foam	Foam, froth, soap lather, whipped cream, beaten egg white, beer, shaving cream	
Gas	Solid	Solid foam	Occluded gases in metals, pumice stone, bread, foam rubber, styrene foam	
Liquid	Gas	Aerosol	Clouds, fog, mist, insecticide sprays.	
Liquid	Liquid	Emulsion	Milk, cream, certain medicines.	
Liquid	Solid	Gel (Solid emulsion)	Curd, cheese, jellies, Fe(OH) ₃ , Al(OH) ₅ butter, boot polish.	
Solid	Gas	Solid foam (Aerosol)	Smoke, dust, fumes	
Solid	Solid	Solid sol	Coloured glasses, coloured precious stones, rock salt, alloys	
Solid	Liquid	Sol	Starch, proteins, As ₂ S ₃ and gold solution, glue, Indian ink, muddy water, milk of magnesia.	

- O Lyophilic sol (Solvent loving): gum, gelatin, starch, albumin
- O Lyophobic sol(Solvent hating): gold sol, silver sol
- O Multi molecular colloids: starch, cellulose, proteins, polymers
- O CMC for soap: 10^{-3} to 10^{-4} mol / lit
- \bigcirc +vely charged sols: hydrated metallic oxides, TiO_2 , haemoglobin, Methylene blue, basic dye
- O -vely charged sols: Metals, Metal sulphides, Acid dyes, eosin, Congo red, starch, gum, gelatin, clay, charcoal
- O Coagulating power α Charge on the ion
- O Gold Number: The minimum number of milli grams of lyophilic colloid required to prevent the coagulation of a standard gold sol on addition of 1 ml of 10% NaCl Solution.

- O Cause of Artificial rain: AgI or electrified sand in contact with cloud
- O flocculation value $\alpha \frac{1}{\text{Charge on ion}}$

eg: $KCl > MgCl_2 > CrCl_3 > SnCl_4$

GENERAL PRINCIPLES OF METALLURGY

- O Froth Collectors: pine oil, sodium ethyl xanthate
- O Froth stabilizers: Cresols, Aniline
- O Depressant: NaCN (prevents ZnS from coming to froth, but PbS comes with froth)
- O Copper Matte: More $Cu_2S + little FeS$
- O Metallurgical transformation:

$$\Delta G = -ve$$
, $\Delta H = +ve$, $\Delta S = +ve$

- O Pig iron: obtained from blast furnace, contains 4% C
- \bigcirc 2Cu₂O + Cu₂S \rightarrow SO₂ + 6Cu (Blister copper)
- O Refining by distillation: Zn, Cd, Hg
 - → Liquation: Sn, Pb, Bi, Hg
 - → Poling: Cu
 - \rightarrow Cupellation: Ag
 - → Electrolytic refining: Cu, Ag, Au, Al, Pb, Zn
 - → **Zone refining:** Ge, Si, B, Ga, In
 - → Vapour phase refining: Ni (Mond's process), Hf & Zr & Ti (Van Arkel Method)
- O Brass: Cu (60 to 80%), Zn (40 to 20%)
- O Bronze: Cu (75 to 90%), Sn (25 to 10%)

- O German silver: Cu (25 to 30%), Zn (25 to 30%), Ni (40-50%)
- O % of C: Pig iron (4%) > Cast iron(3%) > Steel(2.1%) > Wrought iron(0.08%)
- O Cryolite (Na_3AlF_6) : lowers M.P., increases conductivity

Fluorspar(CaF₂): Decreases **F**usion temperature.

p-Block Elements

15 th group:

- O Stability, Basic Nature, Bond Angle: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
- **O M.P:** $NH_3 > SbH_3 > AsH_3 > PH_3$
- **O B.P:** $SbH_3 > NH_3 > AsH_3 > PH_3$
- **O** Hydrolysis of P_4O_6 or PCl_3 gives H_3PO_3
- **Q** Hydrolysis of P_4O_{10} or PCl_5 gives H_3PO_4
- O Anhydride of H_3PO_4 is: $P_4O_{10} \& H_3PO_3$ is: P_4O_6 $(TRICK : 4H_3PO_4 - 6H_2O = P_4O_{10})$ $(4H_3PO_3 - 6H_2O = P_4O_6)$
- O Nessler's reagent: $K_2[HgI_4]$ a mixture of KI, NaOH, HgCl,
- **O Brown ring:** $[Fe(H_2O)_5 NO]SO_4$ Where oxi. state of Fe = +1
- O IUPAC name of brown ring: penta aqua Nitrosonium Iron (I) Sulphate
- Aquaregia: conc HNO₃: con HCl in 1:3 ratio
- O Nitrolim: $CaCN_2$ +graphite (used as fertilizer)
- O Oxo Acids of S:

- O NH_3 dried over: CaO (quick lime)
- O Heating of $Pb(NO_3)_2$ gives O_2 , NO_2 , PbO; NH_4NO_3 gives N_2O ; NH_4NO_2 gives N_2 ; N_2O , gives $NO \& NO_2$.
- O Smoke screens & Holme's signals: combustion of *PH*₃ (produced by *CaC*₂ & CaS).
- O dil.HNO₃ reacts with Cu to give NO whereas *Zn* gives N₂O
- **O Con.HNO**₃ reacts with Cu, Zn, I_2 , C, S_8 , P_4 gives **NO**₂ along with Cu(NO₃)₂, Zn(NO₃)₂, HIO₃, CO₂, H,SO₄, H,PO₄.
- Meta phosphoric acid exists in polymeric form (HPO₃)_n only

16 th group

- **O** Electron gain enthalpy: S > Se > Te > Po > O
- O Electronegativity: O > Se > S > Te > Po
- O Thrust in rockets given by combustion of Hydrazine in liquid O_2
- O Oxi.agent in the manufacture of KMnO4 is O₃
- O SO, is Antichlor, disinfectant, preservative
- As impurities purified by gelatinous Fe₂O₃
- O O_3 oxidises NO_2^- to NO_3^- , SO_3^{-2} to SO_4^{-2} , NO to NO_2 , SO_2 to SO_3 , HX to X_2 (not HF), PbS to $PbSO_4$, Moist I_2 to HIO_3 , Hg to Hg_2O (tailing of Hg)
- For decomposition of O_3 : $\Delta H = \Delta G = -ve \quad \Delta S = +ve$

Thinking order	Writing order	Formula	Name of the acid
(2)	1.	H ₂ SO ₃	Sulphurous acid (+4)
(1)	2.	H_2SO_4	Sulphric acid (+6)
(3)	3.	H ₂ SO ₅	PeroxoMono Sulphuric acid (+6)
(5)	4.	$H_2S_2O_2$	Thionous acid (-2, +4)
(7)	5.	$H_2S_2O_3$	Thionic acid (-2,+6)
(6)	6.	$H_2S_2O_4$	DiThionous acid (+3, +3)
(10)	7.	$H_2S_2O_5$	Pyro Sulphurous acid (+3, +5)
(8)	8.	$H_2S_2O_6$	Di thionic acid $(+5, +5)$
(11)	9.	$H_2S_2O_7$	Pyro Sulphuric acid (+6, +6)
(4)	10.	$H_2S_2O_8$	Peroxo di sulphuric acid (+6, +6)
(9)	11.	$H_2S_{n+2}O_6$	Poly thionic acid(0,+5)

O Charring of sugar is dehydration reaction

$$C_{12}H_{22}O_{11} \xrightarrow{conc.H_2SO_4} 12C + 11H_2O$$

O Cyclic trimer of SO_3 has 6S = 0 & 3S - O - Sbonds

17th GROUP

- **O** Oxidising power: $Cl_2O > ClO_2 > Cl_2O_4 > Cl_2O_7$
- O Acidic Nature: $Cl_2O_7 > Cl_2O_6 > ClO_2 > Cl_2O$
- O Bond angle: $HClO_2 > HClO_4 > HClO_3 > HClO$
 - (111^{0}) $(109 \cdot 5^{0})$ (106^{0}) (90^{0})
- O reducing power: $I^- > Br^- > Cl^-$
- O Acid strength of oxyacid α No. of Oxygens
- **O** Acid strength: $H_{\gamma}Se > HI > HBr$
- O pseudohalide: CN
- O Tincture of Iodine: alcoholic Solution of I_2
- O Iodised salt prepared from: KI & KIO₃
- O Spent Nuclear fuel PuF_6 removed by: O_2F_2
- O Bleaching agent in paper industry: Cl O₂
- \bigcirc CO can be estimated by: I_2O_5
- O Bond disso. energy: $Cl_2 > Br_2 > F_2 > I_2$
- O Litmus paper is decolourised by chlorine water due to **bleaching action** of *HOCl*.
- O XX_3 ' are Bent T-shaped, XX_5 ' are square pyramidal
- O Poisonous gases: phosgene (COCl₂), tear gas (CCl_3NO_2) , mustard gas $(ClCH_2CH_2)$, S
- O reaction of Cl, with cold, dil NaOH gives NaCl, NaOCl, but hot, conc.NaOH gives NaCl & NaClO₂.
- O enrichment of U^{235} is done by CIF_3 or BrF_3 .

18th GROUP

- He can diffuses through rubber, glass, plastic
- O liquid *He* used in: Nuclear reactors, NMR, MRI.
- O $XeF_2 + 2H_2O \rightarrow 4HF + 2Xe + O_2$ $6XeF_4 + 12H_2O \rightarrow 24HF + 4Xe + 2XeO_3 + O_2$

 $XeF_6 + 1H_2O \rightarrow 2HF + XeOF_4$

 $XeF_6 + 2H_2O \rightarrow 4HF + XeO_2F_2$

 $XeF_6 + 3H_2O \rightarrow 6HF + XeO_3$

O Mixture of 0,+He: used by deep sea divers &

- asthma patients
- O Solubility & ease of liquifaction & enthalpy of vaporisation : Xe > Kr > Ar > Ne > He
- O % of d character: $XeF_6 > XeF_4 > XeF_2$
- O Rn: used in the treatment of cancer
- O Ne: used in Beacon lights, decorative discharge tubes
- O Kr-85: used in electronic tubes
- Ar+Hg Vapour: used in fluoroscent tubes
- O $C_p/C_v = 1.66$ for noble gases (Mono atomic)

compound	No. of Lone pairs	No. of σ bonds	No. of π bonds	Hybridization
XeF ₂	3	2	0	sp³d¹
XeF ₄	2	4	0	sp³d²
XeF,	1	6	0	sp³d³
XeO ₃	1	3	3	sp ³
XeO ₄	0	4	4	sp ³
XeOF ₄	1	5	1	sp ³ d ²
XeO ₂ F ₂	1	4	2	sp ³ d ¹
XeOF ₂	2	3	1	sp³d¹

CHEMISTRICK:

No. of L.P.S =
$$\frac{G - (No. of F + 2 \times oxygens)}{2}$$

No. of \sigma = No. of F + No. of oxygens

No. of $\pi = No.$ of oxygens

d & f BLOCK ELEMENTS & CO-ORDINATION **COMPOUNDS**

CHEMISTRICK "ScanTi Vecro Man ICoNi

(Sc, Ti, V, Cr, Mn, I = Iron Ferrum, Co, Ni, Cu, Zn)

- O $\mu = \sqrt{n(n+2)}$ B.M.
- $\mu = n + 0.7 \text{ or } 0.8 \text{ or } 0.9.$

n = no. of electrons = $\mu - 0.7$ or 0.8 or 0.9

- \bigcirc E.A.N.= Z oxi.No. + 2× unidentate ligands
- $\Delta_t = \frac{4}{9} \Delta_0$
- O If $\Delta_0 > P$ (Weak field ligands) if $4e^-$ are there

- O If $\Delta_0 < P$ (strong field ligands) if $4e^-$ are there $t_{2g}^3 e_g^1$
- O Weak field ligands: H_2O , halides, OH⁻, S⁻², $C_2O_4^{-2}$ can form outer orbital complex with formula $ns^x np^y nd^z$

(Where x + y + z = coordination Number) (n = principal quantum number)

eg:
$$[CoF_6]^{-3} = s^1 p^3 d^2$$

- O Strong field ligands: NCS^- , en, CN^- , CO can form inner orbital complex with formula $(n-1)d^x ns^y np^z$
- O **Note**: some times *x* could be zero

principal quantum num

POLYMERS

eg:
$$[Fe(CN)_6]^{-4} = d^2s^1p^3$$

O Spectro chemical series (order of Δ or CFSE):

$$I^{-} < Br^{-} < S^{-2} < SCN^{-} < Cl^{-} < N^{-3} < F^{-}$$

 $< OH^{-} < C_{2}O_{4}^{-2} < H_{2}O < NCS^{-} < NH_{3}$
 $< en < CN^{-} < CO$

- O Overall stability constant $\beta_n = K_1 \cdot K_2 \cdots K_n$
- O Instability constant $=\frac{1}{\beta_n}$

CHEMISTRICK for 14 Lanthanoids
"LaCe is Predominantly Needed to Promote
Same European God's Terrible, Dynamic,
Honourable Erratic TommYbLue".

S.No	Polymer	Monomers	Special features
1.	Nylon-6 (perlan-L)	Caprolactam	polyamide, condensation, homopolymer
2.	Nylon 6, 6	adipic acid & hexamethylene diamine	polyamide, condensation, copolymer, fibre
3.	Nylon-2 Nylon-6	glycine & caproic acid	polyamide, condensation, copolymer, Biodegradable
4.	PHBV	3-hydroxy butanoic acid, 3- hydroxy pentanoic acid	polyamide, condensation, copolymer, Biodegradable
5.	Bakelite	Phenol & HCHO	polyamide, copolymer, Novolac (initial product)
6.	Terylene (Dacron/PET)	Terepthalic acid & ethylene glycol	polyster, fiber, condenstion, copolymer
7.	Teflon	Tetra Fluoro ethene	HDPE, homopolymer, Non sticky, addition
8.	Neoprene	Chloreprene	homo, addition, elastomer, synthetic rubber
9	Buna - N	1, 3 Buta diene, Acrylonitrile (vinyl cyanide)	Elastomer, synthetic rubber, copolymer
10.	Buna - S	1, 3 Buta diene, styrene	Elastomer, synthetic rubber, copolymer
11.	Poly Acrylonitrile	Vinyl cyanide	Addition, homopolymer, HDPE, present in fibres like orlon, acrilan
12.	Glyptal	Ethylene glyeol & Pthalic acid	condensation, polyester, copolymer, used in paints

O Ziegler Natta catalyst:

 $(C_2H_5)_3Al + TiCl_4$ used to get HDPE

$$O PDI = \frac{\overline{M}_w}{\overline{M}_n}$$

BIOMOLECULES

CHEMISTRICK: Mono remala weds Noresu Reducing sugars: maltose, lactose, all mono saccharides

Non reducing sugars: sucrose

Anomers: $\alpha - D$ glucose & $\beta - D$ glucose

Glycogen: structure is similar to amylopectin, highly branched present in liver, brain, muscles, yeast, fungi.

- O Essential Amino acids: obtained through diet (CHEMISTRICK TV FILMWHRK is essential) they are Threonine, Valine, F-phenyl alanine, Isoleucine, Methionine, W- trypophan, Histidine, R-Arginine, K-Lysine
- O Proline has secondary amino (imino) group
- O Except glycine all other natural amino acids are optically active.
- O Peptide bonds are present in **proteins** & **enzymes**
- O Insulin Contain 51 amino acids
- O Insulin, albumins, haemoglobin, enzymes are globular proteins
- \bigcirc 2°, 3° structure of **proteins**: consists H-bonds, - S - S - bonds, electrostatic forces of attraction and Van der Waals forces.
- O During denaturation of proteins only 2° & 3° structures are destroyed
- \bigcirc expect B_1 , others B_1 , B_2 , B_6 are excreted in urine CHEMISTRICK UR TireD

CAGU: RNA CAGT: DNA

Purine bases: Adenine (A), Guanine (G) Pyramidine bases: Cytosine (C), Uracil (U), Thymine (T)

CHEMISTRICK: CUT the Pyramid

- O Nucleoside: Base + Pentose sugar
- O Nucleotide: Base + Pentose sugar + Phosphate
- O Steroid hormones: estrogens, androgens
- O Poly peptide hormones: glucagon, insulin, endorphins
- O Amino acid derivative hormones: Thyroxine [contains iodine], epinephrine, norepinephrine
- O Insulin: decrease the glucose level (by converting glucose to glycogen)
- O Glucagon: increase the glucose level into glycogen

Low level of thyroxine: Leads to hypothyroidism (lethargyness & obesity)

Characters of Addison's disease: stress, weakness, hvpoglycemia

O Hormone produced during stress: Adrenaline

Sucrose = $\alpha - D$ - glucopyranose + $\beta - D$ fructotfuranose

- O Mutarotation: exhibited by reducing sugars (in hemiacetal & hemiketal forms)
- O Chirality of DNA & RNA: due to D-sugar content Helical structure of protein

Hydrogen bonding

No of Chiral Carbons in $\alpha - or \beta - D$ - glucose: 5

In **DNA**: A = T: G = C

O Complimetary strand of TATGACTG of DNA is ATACTGAC; RNA is AUACUGAC CHEMISTRY IN EVERYDAY LIFE

- O Deltol: Mixtrue of Terpineol & Chloroxylenol, used as antiseptic
- O Antiseptic: Bithional, 0.2% phenol
- O Stable artificial sweetener: Alitame
- O Antihistamines: Diphenyl hydramine, promethazine, brompheniramine (Dimetapp), terfenadine (seldane)
- O Tranquilisers: Valium, Equanil, noradrenaline, Luminal, seconal
- O Aspirin: Acetylation product of O-hydroxy benzoic acid, it is antipyretic & analgesic
- O Antacids: $NaHCO_3$, $Al(OH)_3$, $Mg(OH)_2$, omeprazole, Lansoprazole, Ranitidine (zantac)
- O Analgesics:
 - → Non-Narcotic: Novalgin, Aspirin, Ibuprofen
 - → Narcotic: Morphine, Heroin, Codeine
- O Antibiotics: (Salvarsan, Prontosil, Sulphanilamide, Azo dye)
 - → Bactericidal: ofloxacin, pencillin
 - → **Bateriostatic:** Tetracycline, chloramphenicol, erythromycin
- O Antiseptics: Dettol, SO_2 , 0.2% phenol, Cl_2 , Bithional, H_2O_2 , Boric acid, CHI_3
- O Antifertility drugs: Norethindrone, Novestrol, Mifepristone
- Antioxidants: BHT, BHA, SO,
- O Food preservatives: Sugar, Vegetable oils, NaCl, C_6H_5COONa
- Order of Sweetness of Artificial Sweetners: Alitame > Sucrolose > Saccharin > Aspartame

- **O Scum:** Insoluble soap $(C_{17}H_{35}COO)_2Ca$ or Mg
- O Shaving Soap: glycerol + rosin
- O Laundry Soap: sodium rosinate + sodium silicate + $\frac{1}{2}$ (4) $C_6H_5COOH > C_6H_5CH_5COOH > \frac{1}{2}$ Sodium carbonate + Borax
- Anionic detergent: sodium lauryl sulphate
- O Cationic detergent: Cetyltrimethyl Ammonium bromide (present in hair conditioner)
- O Non ionic detergent: Liquid dish washing detergent
- O Biodegradable detergent: unbranched hydrocarbons
- O Non biodegradable detergent: branched hydrocarbons

ORGANIC CHEMISTRY

Orders:

O Dipole moment:

$$CH_3Cl > CH_3F > CH_3Br > CH_3I$$

- O B.P.: Phenol > Water > alcohol (CHEMISTRICK: The great pheno Waal like the great china wall)
- **Q B.P.** of dichloro Benzene: o > p > m**M.P.** of dichloro Benzene: p > o > m
- O SN 1:

 $3^{\circ} RX > 2^{\circ} n - butylX > 2^{\circ} isobutylX > 1^{\circ} RX$ SN²:

$$3^{0} RX < 2^{0} n - butylX < 2^{0} isobutylX < 1^{0} RX$$

O SN 1:

 $Ar_{2}CRX > Ar_{2}CHX > ArRCHX > ArCH_{2}X$

 $Ar_2CRX < Ar_2CHX < ArRCHX < ArCH_2X$ $(R = alkyl, Ar = (C_cH_c)Aryl, X = halide)$ CHEMISTRICK Two In One (SN²- Inversion-One step)

- Order of **dehydration** of alcohols: $3^{\circ} > 2^{\circ} > 1^{\circ}$
- Order of **reactivity** of alcohols with HX:

$$3^{0} > 2^{0} > 1^{0}$$

Order of reactivity

(1) $RCOCl > (RCO)_2O > RCOOR > RCOOH$

 $> RCONH_2$

- (2) Alkene > alkyne > alkane
- (3) RCHO > RCOR
- O Acidic nature
- (1) picric acid > 3, 5 dinitro phenol > 0 nitro phenol> m- nitro phenol > phenol > m - cresol > p- cresol > o - cresol
- (2) $1^{0} OH > 2^{0} OH > 3^{0} OH$

- (3) p- nitro phenol > o nitrophenol > m-nitrophenol > Phenol.

$$CH_3COOH > C_2H_5COOH$$

(5) $-CF_3 > -NO_5 > -CN > -F > -Cl > -Br$

$$> -I > -C_6 H_5$$

(6)
$$p->o->m-> 0$$

 $(e^-.W.D. groups$

(e⁻. Donating groups

are substituted)

are substituted)

Basic Nature:

(1) In gaseous state:

$$3^{0} - NH_{2} > 2^{0} - NH_{2} > 1^{0} - NH_{2} > NH_{3}$$

(2) In aqueous state:

$$R_2NH > RNH_2 > ArCH_2NH_2 > NH_3 >$$

 $ArNHR > ArNH_1 > ArNR_1$

- (3) $(CH_3)_2 NH > CH_3 NH_2 > (CH_3)_3 N > NH_3$
- $(4) (C_2H_5)_2NH > (C_2H_5)_2N > C_2H_5NH_2 > NH_2$

(5)
$$p - > o - > m - > \bigcirc$$
 $> m - > -p - > o - \bigcirc$

 $(e^{-}.Donating\ groups$ $(e^-.W.D. groups$ *are substituted*) are substituted)

(6)
$$R-N>H-N>R-N>H-N>NH_3$$

 \bigcirc -Cl is o - & p - directing

But -NO, group shows its effect only at o- and ppositions (though it is *m*-directing)

- O In coupling BDC reacts with PhenOl to give Orange dye, whereas Aniline gives An yellow dye
- **Ozonolysis:** break = bond or \equiv bond put oxygen before & after the bond to get the products.

O Names of series of Oxyacids in order: CHEMISTRICK OMSGAP. Oxalic acid, Malonic acid, Succinic acid, Glutaric acid, Adipic acid, Pimelic acid

Purpose of reagents:

- O Hydration (+H,O): $HgSO_4 + dil.H_2SO_4$
- **O Dehydration** $(-H_2O)$: $conc \cdot HgSO_4 + Heating$ at $170^{\circ} C(or) P_{1}O_{10}(or) Al_{2}O_{2} + Heating up to 350^{\circ} C$
- O Dehydrohalogenation(-HX): alc.KOH
- O Dehalogenation(-X): Zn dust
- O Reduction $(+H_2)$: $Zn Cu + C_2H_5OH$ (or) Zn - $Hg + conc.HCl(or)H_2N - NH_2(or)H_2/Ni$ (or) Pt (or) Pd; $HI / Red P_A$; $LiAlH_A$; $NaBH_A$
- O Partial reduction $(+H_2): H_2 + Pd / BaSO_4$ in quinoline
- O **Oxidation** $(+O \ or -H_2)$: Alk.KMnO₄ (or)acidified $K_2Cr_2O_7$ (or) Cr_2O_3 / H_2SO_4
- **O** Partial reduction $(-H_2)$: PCC or PDC
- O Hydroboration oxidation: to convert alkene to alcohol

$$B_2H_6 + H_2O_2 + aq.NaOH$$

- **O Decarboxylation:** $(-CO_2)$: NaOH + CaO + Heat
- O Halogenation $(+X): X_2 / h.v.$ (sunlight) (or) Cl₂ / FeCl₃ (or) Br₂ in CH₃COOH (or) Br₂ in CS_2 at 0° C
- O α Halogenation (+X at α carbon): $Cl_2 + \text{Red } P_4$
- O Nitration (substitution of $-NO_2$): $Conc.HNO_3 + Conc.H_2SO_4$ (or) KNO_2 / DMF Sulphonation (sub. of $-HSO_3$): conc. $H_2S_2O_7$ (oleum)
- O Alkylation (sub. of -R): RX & Anhyd. AlX,
- O Acylation(sub.of-COR): RCOX & Anhyd. AlX,
- O Aldol condensation: dil. NaOH
- **O** Ketol condensation: Ba(OH),
- O Cannizzaro condensation (For aldehydes does not contain $\alpha - H$): KOH or NaOH
- O Hydrolysis of CN: $\begin{array}{c} C & N \\ O & H_2 \longrightarrow -COOH + NH_3 \\ H & H \end{array}$

Hydrolysis of NC:
$$\begin{array}{c} N \\ H \\ OH \\ \end{array} \longrightarrow NH_2 + HCOOH$$

- O Alkaline KMnO₄ (Baeyer's reagent): To detect unsaturation & oxidation
- \bigcirc Red P_A + conc HI: To reduce CHO, CO,

$$-COOH$$
, $-CH_2OH$ to $-CH_3$

- \bigcirc ZnHg + conc.HCl: To reduce CO to CH₂
- **O Removal of** $-CO: Br_2 + KOH$
- O Distinguish 10, 20, 30 Alcohols: ZnCl₂+Conc.HCl
- O Distinguish aldehydes from ketones:
 - **❖ Tollen's reagent** (Ammonical AgNO₃)
 - **❖ Fehling's solution**(alk. CuSO₄ + sodium potassium tartarate)
 - Schiff's reagent: decolouration of rosaniline hydro chloride with SO_2 .
 - **❖ Benedict's Solution:** alk CuSO₄ + sodium potassium citrate
- O To neutralise acid: pyridine

Named reactions:

O Hydroboration-oxidation:

$$\begin{split} H_3C-CH = CH_2 &\xrightarrow{1)B_2H_6} \\ &\xrightarrow{2)H_2O,H_2O_2,NaOH} & \\ &CH_3CH_2CH_2OH \end{split}$$

TRICK:

- (1) Addition of water
- (2) Follow Anti Markovnikov rule
- O Esterification: $CH_3COOH + HOH_5C_2 \xrightarrow{H^+}$ $CH_3COOC_2H_5 + H_2O$
- O Kolbe's:

$$C_6H_5OH \xrightarrow{1)NaOH} C_6H_5(OH) COOH$$

O Reimer - Tiemann:

$$C_6H_5OH \xrightarrow{1) CHCl_3} C_6H_5(OH) CHO$$

[Intermediate: Benzalchloride; Intermediate species: dichlorocarbene(:CCl2)]

O Williamson's:

$$C_2H_5Cl + C_2H_5ONa \rightarrow C_2H_5OC_2H_5 + NaCl$$

O Rosenmund's:

$$C_6H_5COCl + H - H \xrightarrow{Pd} C_6H_5CHO + HCl$$

- O Stephen: $CH_3CN \xrightarrow{1) SnCl_2, HCl} CH_3CHO + NH_3$
- O Etard:

$$C_6H_5CH_3 \xrightarrow{1) CrO_2Cl_2, CS_2} C_6H_5CHO$$

O Gattermann-Koch:

$$C_6H_6 \xrightarrow{1) CO, HCl} C_6H_5 \cdot CHO$$

O Clemmensen:

$$CH_3COCH_3 \xrightarrow{ZnHg} CH_3CH_2CH_3 + H_2O$$

O Wolff-Kishner:

$$\begin{array}{c} CH_{3}COCH_{3} \xrightarrow{NH_{2}NH_{2}} (CH_{3})_{2}C = NNH_{2} \\ \xrightarrow{KOH, \ ethylene \ glycol} CH_{3}CH_{2}CH_{3} + N_{2} \end{array}$$

O Cannizzaro:

$$H \longrightarrow C = O + H \longrightarrow C = O \xrightarrow{Conc. KOH} CH_3OH + HCOOK$$

O H.V.Z.:

O Finkelstein:

$$CH_3Cl + NaI \xrightarrow{dry \ ether} CH_3I + NaBr$$

- O Swarts: $CH_3Br + AgF \rightarrow CH_3F + AgBr$
- O Saytzeff:

O Wurtz:

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{dry \ ether}$$

$$CH_3CH_4 - CH_4 + 2Na)$$

$$CH_3 - CH_3 + 2NaBr$$

O Fitting:

$$C_6H_5Br + 2Na + BrC_6H_5 \xrightarrow{dry \ ether}$$

 $C_6H_5C_6H_5 + 2NaBr$

O Wurtz Fitting:

$$C_6H_5Br + 2Na + BrCH_3 \xrightarrow{dry\ ether}$$

$$C_6H_5CH_3 + 2NaBr$$

O Gabriel pthalimide:

$$C_6H_4(CO)_2NH \xrightarrow{i) alc.KOH} ii) RX, \Delta$$
 $iii) aa.NaOH$

$$C_6H_4(COONa)_2 + RNH_2(aliphatic)$$

O Hoffmann bromamide degradation:

$$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2$$

 $+2NaBr + Na_2CO_3 + 2H_2O$

O Diazotisation:

$$CH_3NH_2 + HNO_2 \xrightarrow{NaNO_2} CH_3N_2Cl$$

$$\xrightarrow{H_2O} CH_3OH + N_2 + HCl$$

O Sandmeyer:

$$C_6H_5N_2Cl + HBr \xrightarrow{Cu_2Br_2} C_6H_5Br \\ +N_2 + HCl$$

O Gatterman:

$$C_6H_5N_2Cl + HCl \xrightarrow{Cu} C_6H_5Cl + N_2 + CuCl$$

O Carbyl amine:

$$C_6H_5NH_2 + CHCl_3 + 3KOH$$

$$\xrightarrow{\Delta} C_6H_5NC + 3KCl + 3H_2O$$

O Idoform:

$$CH_3CHO + 4KOH + 3I_2 \rightarrow CHI_3$$

+ $HCOOK + 3KI + 3H_2O$

O Aldol Condensation:

$$CH_{3} - C + H - C - CHO \xrightarrow{Dil.NaOH}$$

$$H \qquad H$$

O Cross Aldol Condensation:

$$CH_{3}CHO + C_{2}H_{5}CHO \xrightarrow{1)NaOH \atop 2)\Delta} \rightarrow$$

$$But - 2 - enal +$$

$$Pent - 2 - enal +$$

$$2 - Methyl \ But - 2 - enal +$$

$$2 - Methyl \ pent - 2 - enal$$

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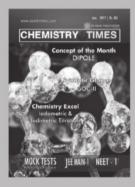
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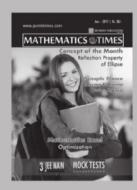
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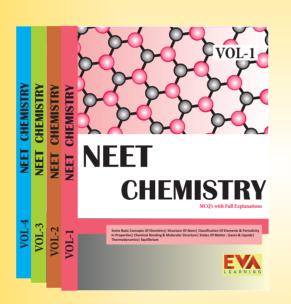
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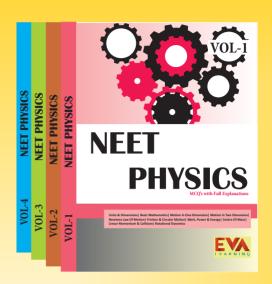


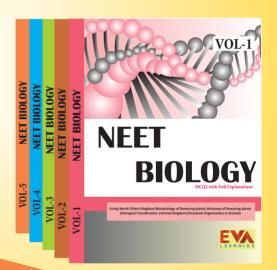
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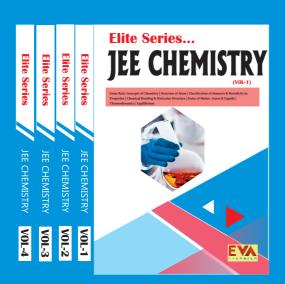
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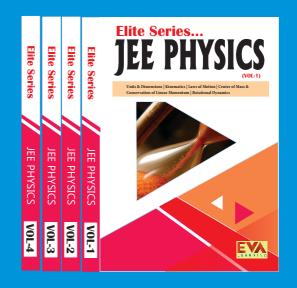


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